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Donor-Acceptor Molecular Figure-of-Eights

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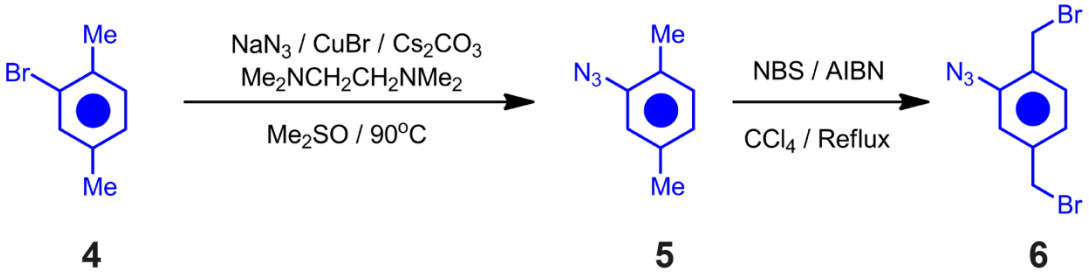
S1. Syntheses

All reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without further purification with the exception of *N*-bromosuccinimide which was recrystallized[S1] from boiling water. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-F254 (Merck 5554). Flash column chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. Compound purification was performed on a preparative RP-HPLC instrument (Shimadzu LC-8A), using a C18 column (Agilent, 10µm packing, 30 mm × 250 mm) . The eluents used were MeCN and H_2O, both mixed with 0.1 % (v/v) trifluoroacetic acid (TFA). The detector was set to λ = 254 nm. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on Bruker Avance III 500 and 600 MHz spectrometers, with working frequencies of 499.373 and 600.168 MHz for ^{1}H, and 125.579 and 150.928 MHz for ^{13}C nuclei, respectively. All ^{13}C NMR spectra were recorded with the simultaneous decoupling of ^{1}H nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (1.94 ppm for CHD_2CN, 7.26 ppm for $CHCl_3$). Electrospray Ionization (ESI) mass spectrometer.

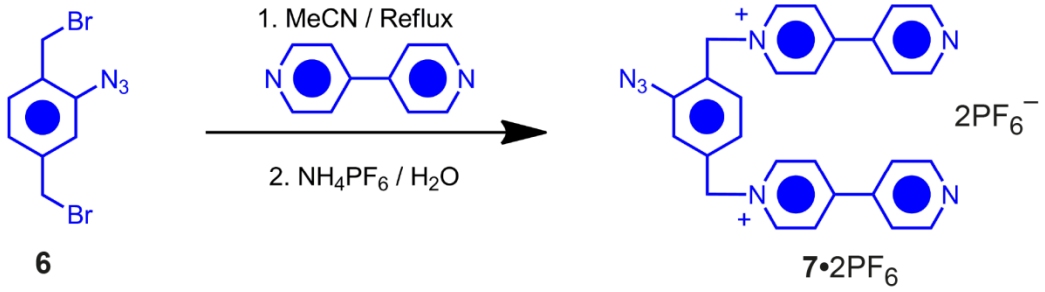


Scheme S1. Synthesis of precursor compound **6**.

2-Azido-*p*-xylene (5). Compound **5** was prepared using a modified procedure developed by Molander *et al*.[S2] Commercially available 2-bromo-*p*-xylene (**4**) (10.0 g, 7.5 mL, 54 mmol), NaN_3 (3.51 g, 54 mmol), CuBr (775 mg, 5 mmol), Cs_2CO_3 (8.80 g, 27 mmol), and *N*,*N*′-

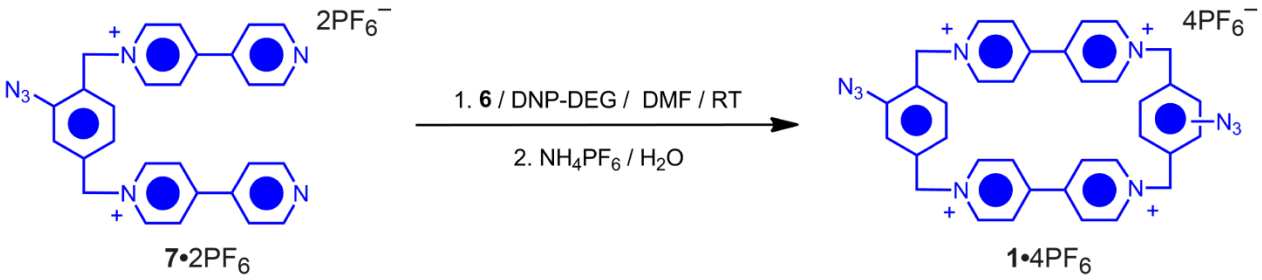
dimethylethylenediamine (952 mg, 1.2 mL, 11 mmol) were combined in dry Me_2SO (500 mL) and the solution was heated to 90°C with stirring. After 12 h, H_2O (500 mL) was added and the product was extracted with CH_2Cl_2 (400 mL x 3). Solvent was removed *in vacuo* and the product was purified by column chromatography [SiO_2 : Hexanes]. The fractions containing the product were combined and the solvent was removed *in vacuo* to yield the azide **5** as a yellow oil (3.50 g, 44%). ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ = 2.17 (s, 3H), 2.34 (s, 3H), 6.85 (d, ^3J = 7.7 Hz, 1H), 6.93 (s, 1H), 7.04 (d, ^3J = 7.7 Hz, 1H) ppm. The ^{1}H NMR spectrum of the product matches that previously reported.[S3]

Dibromide 6 was prepared from **5** according to a literature procedure.[S3]



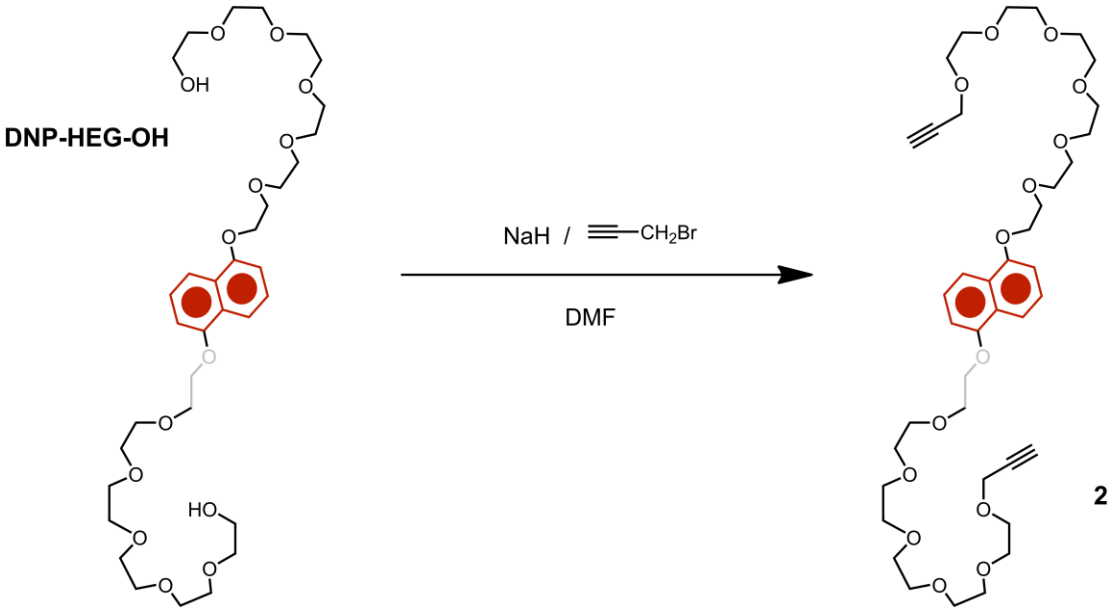
Scheme S2. Synthesis of dicationic cyclophane precursor **7**•2PF_6.

Dicationic Precursor 7•2PF_6**.** Dibromide **6** (300 mg, 0.9 mmol) and 4,4'-bipyridine (922 mg, 5.9 mmol) were combined in MeCN (50 mL) and heated under reflux for 12 h. The crude reaction mixture was filtered, the residue dissolved in H_2O (200 mL), and the crude product precipitated by the addition of NH_4PF_6. Column chromatography [SiO_2 : 2M NH_4Cl / MeOH / $MeNO_2$ (12 : 7: 1)] was employed to obtain **7**•2PF_6 as a white solid (735 mg, 94%). ^{1}H NMR (CD_3CN, 500 MHz, 293 K): δ = 5.67 (s, 2H), 5.78 (s, 2H), 7.35 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H), 7.51 (d, ^3J = 1.4 Hz, 1H), 7.68 (d, ^3J = 7.9 Hz, 1H), 7.82 (m, 4H), 8.29 (d, ^3J = 6.9 Hz, 2H), 8.33 (d, ^3J = 6.9 Hz, 2H), 8.86 (m, 8H) ppm. ^{13}C NMR (CD_3CN, 125 MHz, 293 K): δ = 59.6, 62.7, 120.1, 121.8, 121.9, 124.3, 125.6, 126.0, 132.7, 135.2, 136.2, 140.7, 141.4, 141.6, 144.7, 144.9, 150.1, 150.2, 153.9, 154.2 ppm. ESI-MS: calcd for $[M - PF_6]^+$, *m*/*z* = 602.1651, found: *m*/*z* = 602.1660.



Scheme S3. Synthesis of bisfunctionalised cyclophane **1**•4PF_6.

CBPQT^{4+}-Bisazide (1•4PF$_6$). Precursor **7**•2PF$_6$ (120 mg, 0.15 mmol), dibromide **6** (50 mg, 0.15 mmol), and the template — 1,5-bis(ethoxy(ethoxy))dioxynaphthalene (DNP-DEG) (250 mg, 0.75 mmol) — were combined in dry DMF (35 mL) and the solution was stirred at 25°C for 5 days before the solvent was removed *in vacuo*. The crude reaction mixture was stirred in a saturated aqueous solution of NH_4Cl until the residue dissolved, after which it was diluted with H_2O (ca. 400 mL). Liquid–liquid extraction using $CHCl_3$ (2 L) was employed to remove the DNP-DEG template (2 days). The remaining crude product was precipitated by the addition of NH_4PF_6 and purified by column chromatography [SiO_2 : 2M NH_4Cl / MeOH / $MeNO_2$ (12 : 7: 1)] to yield the isomeric mixture of bisazides **1**•4PF$_6$ as an off-white solid (45.5 mg, 25.7 %). ^{1}H NMR (CD_3CN, 500 MHz, 293 K): δ = 5.68 (s, 4H), 5.73 (s, 4H), 7.32 (d, ^3J = 1.55 Hz, 2H), 7.41 (dd, ^3J = 7.81 Hz, ^4J = 1.55 Hz, 1H), 7.42 (dd, ^3J = 7.81 Hz, ^4J = 1.55 Hz, 1H), 7.65 (d, ^3J = 7.81 Hz, 2H), 8.17 (m, 8H), 8.90 (m, 8H) ppm. ^{13}C NMR (CD_3CN, 125 MHz, 293 K): δ = 61.22, 61.25, 65.09, 120.98, 121.04, 127.04, 127.10, 127.69, 127.75, 128.27, 128.33, 133.53, 133.60, 138.62, 138.70, 141.57, 141.61, 146.15, 146.20, 146.68, 146.74, 150.46, 150.57 ppm. ESI-MS: calcd for [M – PF$_6$]$^+$, m/z = 1037.1580, found: m/z = 1037.1579.



Scheme S4. Synthesis of Guest **2**.

DNP-HEG-OH (2-{2-[2-(2-{2-[2-(5-{2-[2-(2-{2-[2-(2-Hydroxy-ethoxy)ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-naphthalen-1-yloxy)-ethoxy}-ehtoxy)-ethoxy]-ethoxy}-ethanol) was prepared according to literature methods.[S4]

Guest 2. NaH (60% in mineral oil, 40 mg, 1 mmol) was added to a solution of DNP-HEG-OH (185 mg, 0.269 mmol) in dry DMF (20 mL) and stirred for 15 min. Propargyl bromide (80% *w*/*w* in PhMe, 0.25 mL, 2.3 mmol) was added slowly, and the mixture stirred for 16 h. MeOH (5 mL) was added carefully to quench remaining NaH, the solvents were removed *in vacuo* to yield a brown oil, which was purified by column chromatography [SiO_2: 5% Me_2CO in CH_2Cl_2] to

yield the product **2** as a light brown oil (137 mg, 0.179 mmol, 66.5%). ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ = 2.43 (t, ^{3}J = 2.3 Hz, 2H), 3.62–3.71 (m, 18H), 3.80 (m, 4H), 3.99 (t, ^{3}J = 5.2 Hz, 4H), 4.19 (d, ^{3}J = 2.4 Hz, 4H), 4.29 (t, ^{3}J = 5.0 Hz, 4H), 6.84 (d, ^{3}J = 7.8 Hz, 2H), 7.34 (t, ^{3}J = 7.8 Hz, 2H), 7.85 (d, ^{3}J = 8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 293 K): δ = 58.5, 68.0, 69.2, 70.0, 70.5, 70.7, 70.7, 70.7, 70.7, 70.7, 70.8, 71.1, 74.7, 79.8, 105.7, 114.7, 125.2, 126.9, 154.4 ppm. ESI-MS: calcd for $[M + Na]^{+}$, *m*/*z* = 782.4364, found: *m*/*z* = 782.4340.

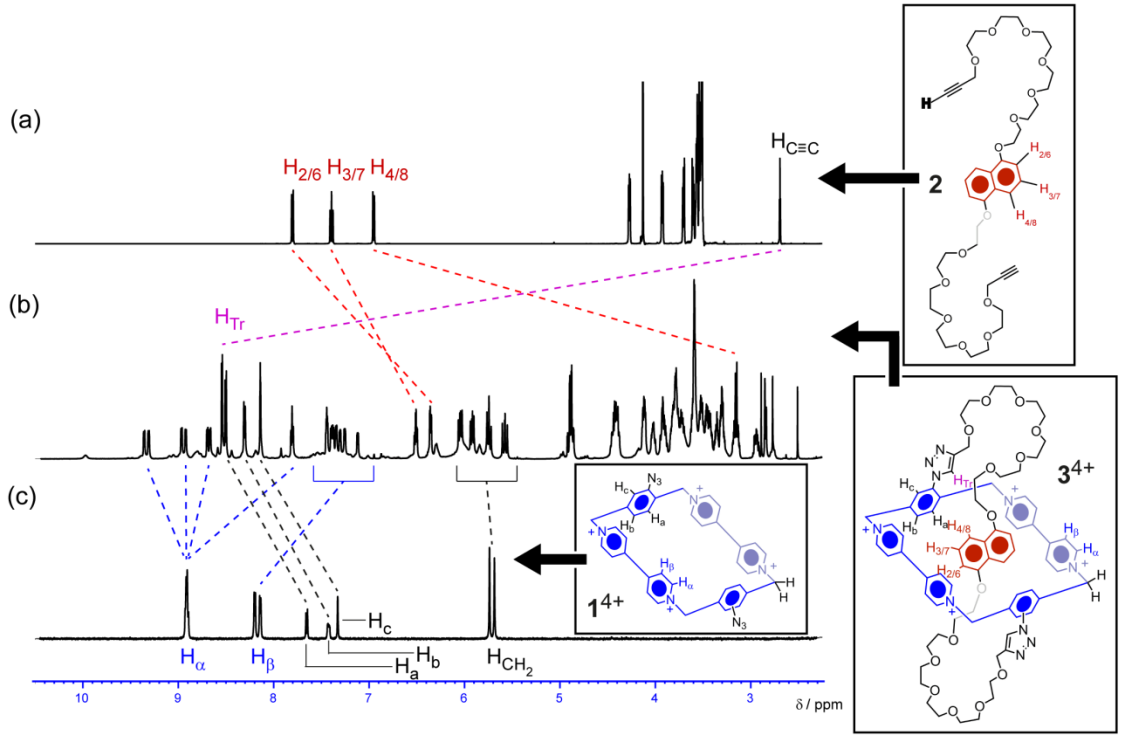


Figure S1. A comparison of the ^{1}H NMR spectra (CD_3CN, 500 MHz, 298 K) of (a) the guest **2,** (b) the Figure-of-Eights **3**•4PF_6 as a mixture of constitutional isomers, and (c) the host **1**•4PF_6 reveals substantial changes in the chemical shifts of the resonances corresponding to protons α and protons β to the nitrogen atoms in the bipyridinium units from $\mathbf{1}^{4+}$ to $\mathbf{3}^{4+}$. Likewise, on going from **2** to $\mathbf{3}^{4+}$, the resonances for the DNP protons experience dramatic upfield shifts – specifically, the signal for the $H_{4/8}$ protons moves from 6.96 ppm in **2** to 2.85 ppm in $\mathbf{3}^{4+}$. Furthermore, the characteristic singlet at 2.69 ppm for the alkyne protons in **2** is replaced by a signal centered at 8.54 ppm in $\mathbf{3}^{4+}$, indicating the successful completion of the Cu-mediated Azide-Alkyne Click (CuAAC) reaction between $\mathbf{1}^{4+}$ and **2** to give $\mathbf{3}^{4+}$.

Figure-of-Eights (**3**•4PF_6). The bisazides **1**•4PF_6 (68.3 mg, 0.06 mmol) and guest **2** (39.7 mg, 0.06 mmol) were degassed in DMF (25 mL) with argon before addition of CuI (1.1 mg, 0.006 mmol) and the solution was stirred for 2 days. Solvent was removed *in vacuo* and the crude product was precipitated from H_2O by the addition of NH_4PF_6 before being purified further using reverse phase high-performance liquid chromatography (RP-HPLC) (H_2O – MeCN / 0 → 40 % in 55 min) to yield a pink solid **3**•4PF_6 as a mixture of constitutional isomers of (13.0 mg, 12% yield). ^{1}H NMR (CD_3CN, 500 MHz, 293 K): δ = 2.85 (d, ^{3}J = 7.8 Hz, 4H), 3.16 (m, 8H), 3.3 –

3.8 (m, 80H), 4.41 (m, 8H), 4.88 (m, 8H), 5.56 (d, ^2J = 14.7 Hz, 2H), 5.59 (d, ^2J = 14.7 Hz, 2H), 5.73 (d, ^2J = 14.7 Hz, 2H), 5.75 (d, ^2J = 14.7 Hz, 2H), 5.91 (d, ^2J = 14.7 Hz, 2H), 5.93 (d, ^2J = 14.7 Hz, 2H), 6.04 (d, ^2J = 14.7 Hz, 2H), 6.05 (d, ^2J = 14.7 Hz, 2H), 6.35 (d, ^3J = 7.8 Hz, 2H), 6.36 (d, ^3J = 7.8 Hz, 2H), 6.51 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 2H), 6.52 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 2H), 7.12 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.26 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.31 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.35 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.38 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.40 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.45 (dd, ^4J = 2.4 Hz, ^3J = 6.8 Hz, 2H), 7.80 (d, ^3J = 6.8 Hz, 2H), 7.82 (d, ^3J = 6.8 Hz, 2H), 8.14 (d, ^4J = 2.5 Hz, 4H), 8.30 (dd, ^3J = 8.5 Hz, ^4J = 2.5 Hz 4H), 8.50 (d, ^3J = 8.5 Hz, 4H), 8.54 (s, 2H), 8.55 (s, 2H), 8.67 (d, ^3J = 6.8 Hz, 2H), 8.70 (d, ^3J = 6.8 Hz, 2H), 8.92 (d, ^3J = 6.8 Hz, 2H), 8.97 (d, ^3J = 6.8 Hz, 2H), 9.31 (d, ^3J = 6.8 Hz, 2H), 9.36 (d, ^3J = 6.8 Hz, 2H) ppm. ESI-MS: calcd for $[M - 2\text{TFA}]^{2+}$, m/z = 796.3169, found: m/z = 796.3214. (^{1}H NMR Spectrum of **3**•4PF_6 stacked with **1**•PF_6 and **2** is shown in Figure S1.) By using iterative HPLC techniques (collection and resubmission through an XBridge Prep C18 OBD 19x100 mm column: H_2O – MeCN / 0 – 60 % in 60 min λ = 254 nm), the *cis* and *trans* isomers were separated in small quantities for NMR spectroscopic analysis — while the single isomers did not resolve into two different peaks, fractions collected from the HPLC showed increasing enrichment of one isomer and repetitive collection and resubmission allowed for approximately 2 mg of each isomer to be collected (Figure S2).

S2. NMR Spectroscopic Assignments to the Two CBPQT^{4+}-Bisazides

During the synthesis of the CBPQT^{4+}-bisazide (**1**•4PF_6) two constitutional isomers, wherein the azide substituents on the *p*-phenylene rings are either both oriented towards (i) the *same* bipyridinium (BIPY^{2+}) unit, i.e., the *cis*–**1**•4PF_6 isomer, or (ii) towards the *opposing* BIPY^{2+} units, i.e., the *trans*–**1**•4PF_6 isomer, are obtained. The relative orientations of the *p*-xylylene links are represented in Figure S2 as the averaged conformations observed by both ^{1}H and ^{13}C NMR spectroscopies in CD_3CN at room temperature where the rotation of the *p*-xylylene links is fast on the NMR time-scale.[S5]

This symmetry-averaged representation is akin to the traditional representation of cyclohexane as a hexagon, i.e. although cyclohexane exists primarily as two degenerate chair conformations that are in rapid equilibrium, we choose to represent the six-membered ring as an averaged high energy conformation – namely, a flat hexagon.

In the case of the isomers of **1**•4PF_6 , we take into account the fast rotations of the *p*-xylylene links and represent them such that their *p*-phenylene rings lie coplanar with the average mean planes of the hosts and perpendicular in each case to the planes of the two BPIY^{2+} units. In this averaged conformation, the *cis*-isomer contains a C_2 axis of rotation and two σ_v mirror planes bisecting along the axis, i.e., the *cis*-isomer resides in the point group C_{2v}. Of the eight protons α to the nitrogens, the four on one BIPY^{2+} unit are constitutionally heterotopic with the four on the

other $BIPY^{2+}$ unit. In each $BIPY^{2+}$ unit, there are two pairs of homotopic α-protons and each one of the pairs has an enantiotopic partner: the result is that one expects two sets of resonances for these α-$BIPY^{2+}$ protons. The same kind of analysis holds true for the β-$BIPY^{2+}$ protons and leads to the prediction that there should also be two sets of resonances for these protons. In the case of the six *p*-xylylene protons, there are three homotopic pairs of constitutionally heterotopic protons, giving rise, one can predict, to a total of three resonances. For the eight methylene protons, there are two sets of constitutionally heterotopic methylene groups. In each set, there are two pairs of homotopic protons and each one of the pairs has an enantiotopic partner: the outcome is the prediction that we should observe two singlets.

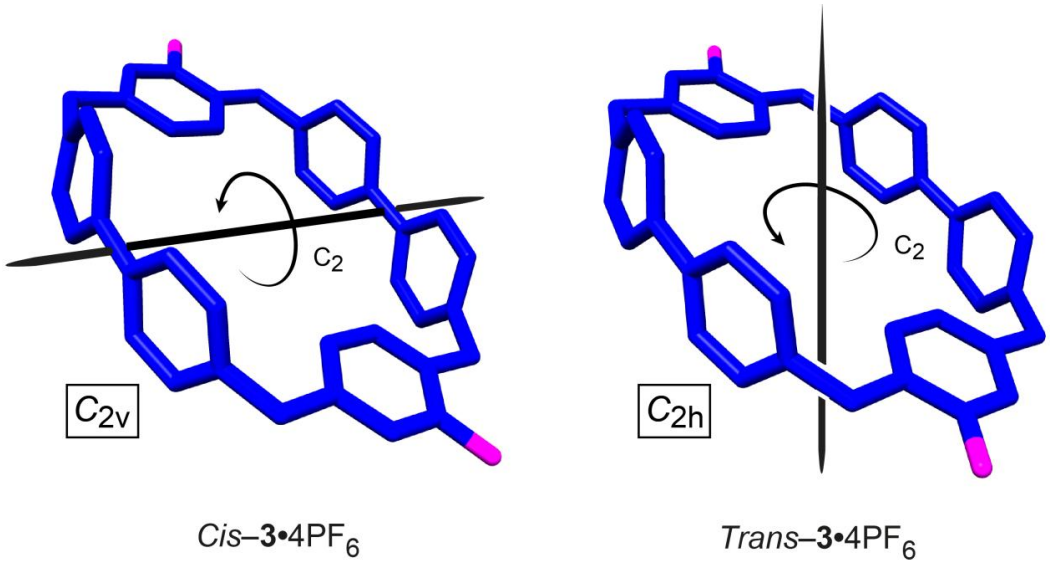


Figure S2. A representation of the two constitutional isomers of **1**•$4PF_6$ as observed by ^{1}H NMR spectroscopy in CD_3CN at room temperature. The rotation of the *p*-xylylenes is fast on the ^{1}H NMR time-scale and thus are represented as flat in the above illustrations. Using these depictions of the averaged conformations, we find that each isomer has a C_2 axis of rotation as shown. Furthermore, the *cis* isomer has two mirror planes σ_v of symmetry through that axis, and thus resides in the C_{2v} point group. The *trans* isomer contains only one mirror plane σ_h perpendicular to the axis as well as a center of symmetry (*i*) and thus resides in the C_{2h} point group. Note that each isomer has the same overall count of resonances expected in the ^{1}H NMR spectra.

By contrast, the *trans* isomer, assuming also an averaged conformation, contains a C_2 axis of rotation and only one σ_h mirror plane in addition to a center of symmetry (*i*). In this isomer, the pyridinium rings in each $BIPY^{2+}$ unit are constitutionally heterotopic, while there are eight pairs of homotopic protons between each of the two $BIPY^{2+}$ units courtesy of the C_2 axis, as well as eight pairs of enantiotopic protons reflected through the σ_h plane and another eight pairs of enantiotopic protons inverted through the center of symmetry (*i*). The net result is the expectation of two resonances for the α-protons and the same holds true, of course, for the β-protons. On the p-xylylene rings, the three constitutionally heterotopic protons are rendered homotopic in pairs by the C_2 axis. Therefore, two resonances are to be expected. For the eight

methylene protons, two sets of methylene groups are constitutionally heterotopic: in each case there are two pairs of homotopic pairs and each one of the pairs has an enantiotopic partner. The analysis leads to the predication of the possible existence of two singlets.

The structural similarities of the two isomers leads to the coincidental overlap of the resonances for the *cis* and *trans* constitutional isomers as observed (Figure S3) at least in the ^{1}H NMR spectrum. The isomers, however, can be identified in the ^{13}C NMR spectrum (Figure S4) where each resonance appears as two peaks (ca. 1:1 ratio) separated by approximately 0.5 ppm from each other.

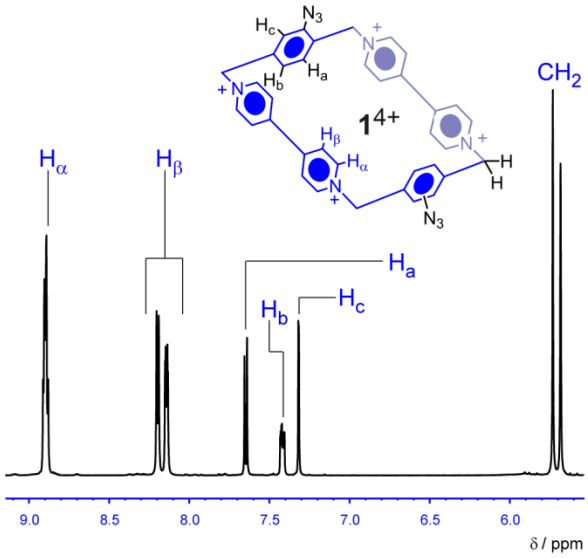


Figure S3. ^{1}H NMR Spectrum of **1**•4PF_6 (500 MHz, 298K, CD_3CN). While both isomers exhibit different symmetries, there is significant overlap of the resonances in the ^{1}H NMR spectrum. Before CuAAC reaction, the isomers cannot be separated or distinguished using ^{1}H NMR techniques.

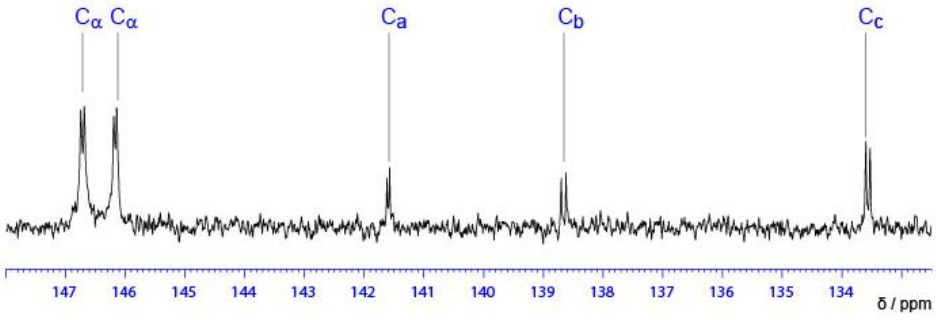


Figure S4. A portion of the ^{13}C NMR spectrum of **1**•4PF_6 (500 MHz, 298K, CD_3CN) is shown in order to demonstrate the appearance of two singlets for each resonance. This observation shows that the constitutional isomers of **1**•4PF_6 are both present after reaction.

S3. X-Ray Crystal Structure of the Bisazides

The presence of the *cis* and *trans* isomers of **1**•4PF_6 is expressed in terms of disorder in the solid state. Crystals were grown by slow vapor diffusion of EtOH into the mixture of *cis*–**1**•4PF_6 and *trans*–**1**•4PF_6 dissolved in DMF. Crystallographically, although at least two isomorphs were observed by unit cell analysis, only one afforded data adequate for refinement.

Data were collected at 100 K using a Bruker d8-APEX II CCD diffractometer (Cu Kα radiation, λ=1.54178 Å). Intensity data were collected using ω and φ scans spanning at least a hemisphere of reciprocal space for all structures (data were integrated using SAINT). Absorption effects were corrected on the basis of multiple equivalent reflections (SADABS). Structures were solved by direct methods (SHELXS[S6]) and refined by full-matrix least-squares against F^2 (SHELXL[6]). Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries, including those bound to oxygen, as no hydrogen atoms could be located in the difference Fourier map. Diffuse, disordered solvent molecules, a mixture of DMF and EtOH, could not be adequately modeled. The bypass procedure in Platon was used to remove the electronic contribution from these solvents. The total potential solvent accessible void volume was 180.6Å^3 and the electron count per cell is 58. As the exact solvent content is not known, the reported formula reflects only the atoms used in the refinement.

The crystal contains the *cis* and *trans* isomers in a ratio of approximately 7:3 of *trans*–**1**•4PF_6 to the non-centrosymmetric *cis*–**1**•4PF_6. The inversion symmetry operation clearly reflects long-range disorder in the organization of the azide groups in this case, thereby allowing non-centrosymmetric *cis*–**1**•4PF_6 to be observed in a centrosymmetric space group.

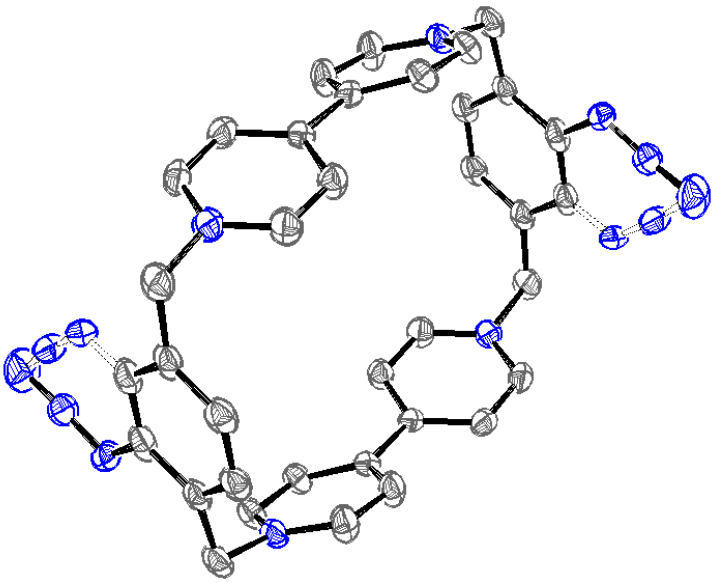


Figure S5. An ORTEP representation of the crystal structure of **1**•4PF_6, with thermal ellipsoids at 50 % probability, showing the disorder in the substitution of the aryl azides. The disorder is noted with one gray and one black bond for the two positional orientations.

Crystal data for **1**•4PF_6: $(C_{36}H_{29}N_{10})_2$•4(PF_6)•2(C_3H_7NO); yellow prism, 0.5 × 0.4 × 0.2 mm^3; triclinic, space group *P-1*; a = 9.858(10), b = 11.991(40), c = 13.986(32) Å; α = 112.320(01), β = 95.706(01), γ = 104.703(01) °; V = 1443.54(3) $Å^3$; Z = 1; ρ_{calcd} = 1.526 gcm^{-3}; $2\theta_{max}$ = 60.64°; T = 100(2) K; 8594 reflections collected, 7301 independent, 519 parameters; μ = 0.255 mm^{-1}; R_1 = 0.0651 [I > 2.0σ(I)], wR_2 = 0.1669 (all data).

S4. NMR Spectroscopic Assignments to the Two Figure-of-Eights

By adding a guest, **2**, and fixing the glycol arms such that *p*-xylene rotation is no longer observed, the isomers of Figure-of-Eight **3**•4PF_6 contain lower symmetries than the isomers of **1**•4PF_6. A similar symmetry argument can be used to account for the number of signals observed in the ^{1}H NMR spectrum and the assignment convention is such that the protons α and β to the nitrogens, the *p*-xylylene protons, as well as the methylene protons are labeled according to their chemical shift in Figure 2 in order from low field to high field. The *cis* isomer of **3**•4PF_6 contains only a C_2 axis of rotation and resides in the C_2 point group. Thus, of the eight protons α to the nitrogens, there are four constitutionally heterotopic pairs of homotopic protons (α_1, α_2, α_3, α_4, Figure S6). Of the eight protons β to the nitrogens, there are four constitutionally heterotopic pairs of homotopic protons (β_1, β_2, β_3, β_4); of the six *p*-xylylene protons, there are three constitutionally heterotopic pairs of homotopic protons (a,b,c); the two triazole protons are homotopic with each other.

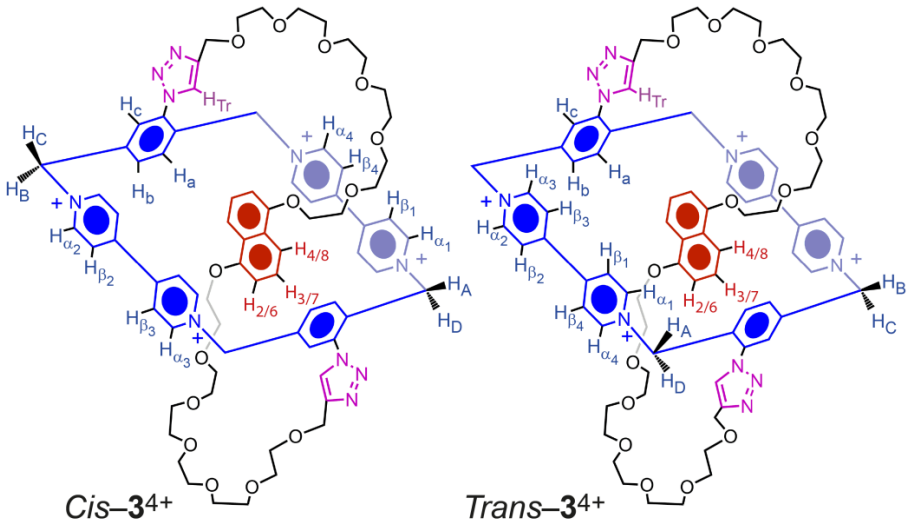


Figure S6. Molecular Figure-of-Eight isomers showing the protons as they are assigned in the ^{1}H NMR spectra (Figure 2, main text). The *cis* isomer contains a C_2 axis of rotation and thus resides in the C_2 point group. The *trans* isomer contains an inversion center and thus resides in the C_i point group. The labeled protons represent sets of homotopic and enantiotopic protons that result in resonances in the ^{1}H NMR

spectra of each isomer.

Furthermore, the *trans* isomer contains only a center of inversion, suggesting *trans*–**3**•4PF_6 resides in the C_i point group. Thus, of the eight protons α to the nitrogens, there are four constitutionally heterotopic pairs of enantiotopic protons such that we observe four resonances (α_1, α_2, α_3, α_4,). Of the eight protons β to the nitrogens, there are four constitutionally heterotopic pairs of enantiotopic protons (β_1, β_2, β_3, β_4); of the six xylylene protons, there are three constitutionally heterotopic pairs of enantiotopic protons (a,b,c); the two triazole protons are enantiotopic to each other. We observe (Figure S1) the same count of resonances in the ^{1}H NMR spectrum of the mixture as predicted by the topicity arguments described herein. Furthermore, recycling HPLC has been employed to separate the constitutional isomers such that the proper count of resonances corresponding to the separated isomers are observed in the ^{1}H NMR spectra (Figure 2).

In the ^{1}H NMR spectra of each isomer, a minor species was observed. Using EXSY experiments, it was observed that the species was most likely in dynamic equilibrium with the major characterized species. Strong chemical exchange correlations were observed as phased positive peaks (black) throughout the EXSY spectrum for each isomer showing the propable dynamic exchange of the Figure-of-Eight with a different conformation.

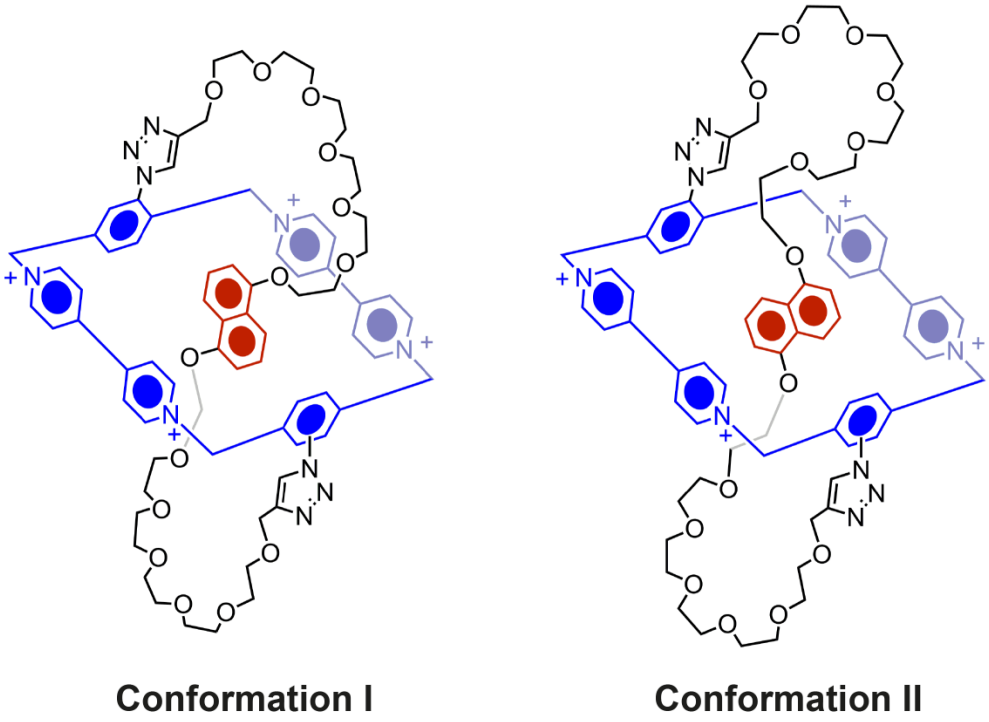


Fig. S7. The two conformations that **3**•4PF_6 is expected to occupy where **Conformation I** is oriented such that the oxygen of the DNP is pointed away from the triazole ring and **Conformation II** is oriented with the oxygen pointed toward the trizole ring. **Conformation I** is the hypothesized major species observed in the ^{1}H NMR spectrum.

While this conformation is currently under experimental investigation, one possible conformation is diagramed in Figure S7 (**Conformation II**). The DNP moiety may occupy two different conformations inside the cavity of the cyclophane (**Conformations I and II**). The two conformations would be in dynamic exchange with each other through a process by which DNP is (i) dislodged from the cavity, followed by (ii) its rotation of 180° around the [O…O] axis, and (iii) reinserted into the cavity.

In previously reported rotaxanes[S7] incorporating DNP and an unmodified $CBPQT^{4+}$, this process is marked by the DNP moiety imposing its local C_{2h} symmetry on the cyclophane such that at room temperature the two conformations are observed by ^{1}H NMR. In our system, the local C_{2h} symmetry of DNP unit should impose two different environments on the $CBPQT^{4+}$-bisazides, but only one conformation is observed as the major species by ^{1}H NMR. Quantum mechanical calculations show that **Conformation I** is preferred over **Conformation II** suggesting that the former is the major species observed in the ^{1}H NMR spectrum. **Conformation II** may possibly represent the minor species observed that is in dynamic equilibrium with the major species.

Assignment of *Cis* and *Trans* Constitutions

In order to differentiate between the two constitutional isomers and assign the two ^{1}H NMR spectra to the *cis* and *trans* isomers, 2D NMR techniques were employed. For *trans*–**3**•4PF_6, the COSY spectrum (Figure S8) displays the scalar couplings between the protons α to the nitrogens in the bipyridinium unit and protons β to the nitrogens in the bipyridinium unit such that each pair corresponds to the protons *ortho* to each other on the bipyridinium units. Furthermore, ^3J couplings between the protons on the dioxynaphthalene (DNP) unit verify the assignment of the DNP unit inside the cyclophane. Finally, ^2J (geminal) couplings for the methylene groups are observed. The same couplings can be observed in the COSY spectrum of the *cis* isomer (Figure S9).

Moving towards the assignment of the isomers, we consider the through-space correlations as observed in the NOESY experiments. For *trans*–**3**•4PF_6 (structure, Figure S6) we first observed the nOes corresponding to the through-space correlations of proton labeled α_1 with xylylene proton a, α_2 with b, and α_3 with c (Figure S10). This observation clarifies the orientation of the bipyridinium protons α to the nitrogen with respect to the aromatic xylylene protons — i.e., $H_{\alpha 1}$ is pointing to the same side of the bipyridinium unit as H_a.

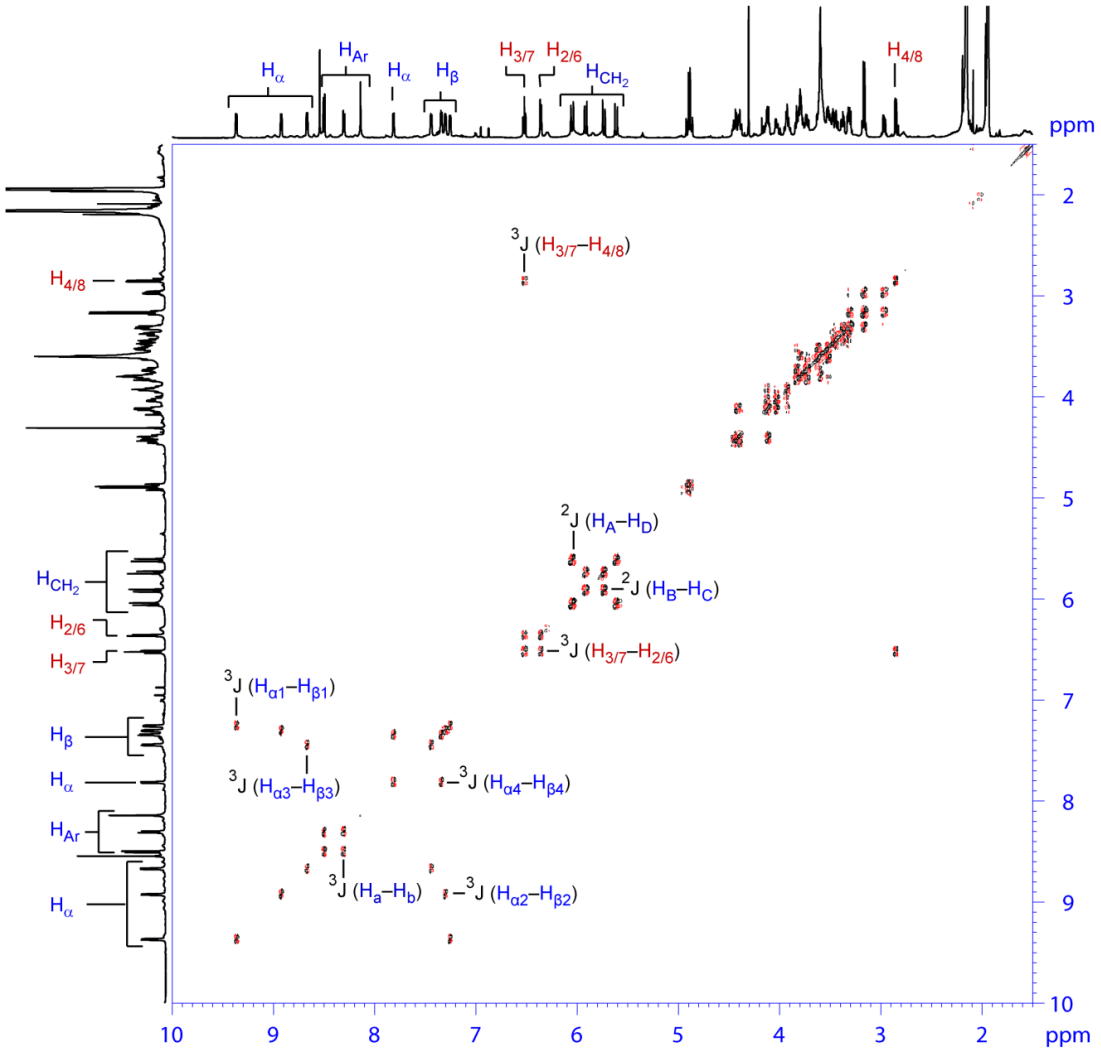


Fig. S8. ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of *trans*–**3**•4PF_6 with selected correlation labeled.

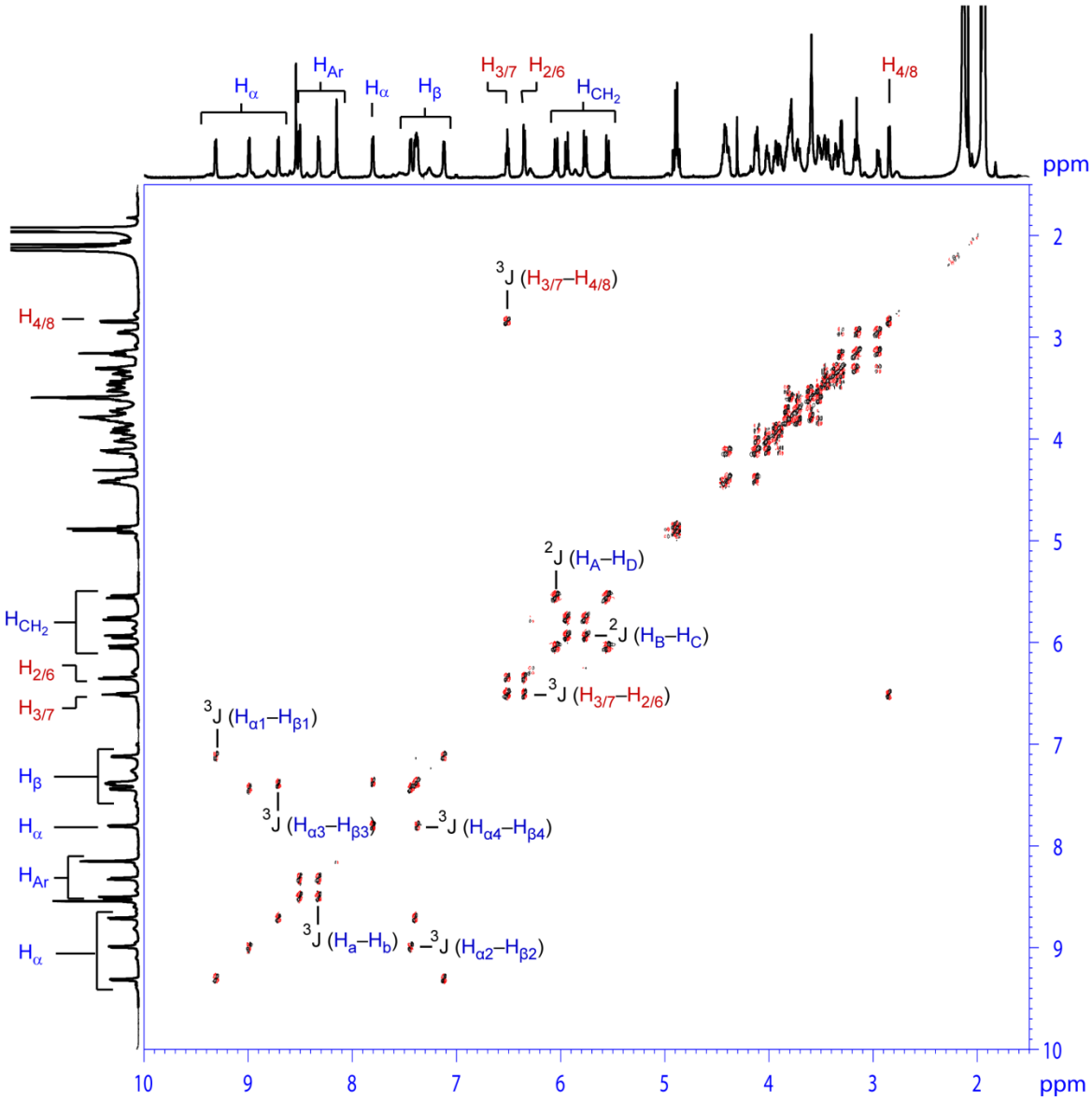


Fig. S9. ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of *cis*–**3**•4PF_6 with selected correlations labeled.

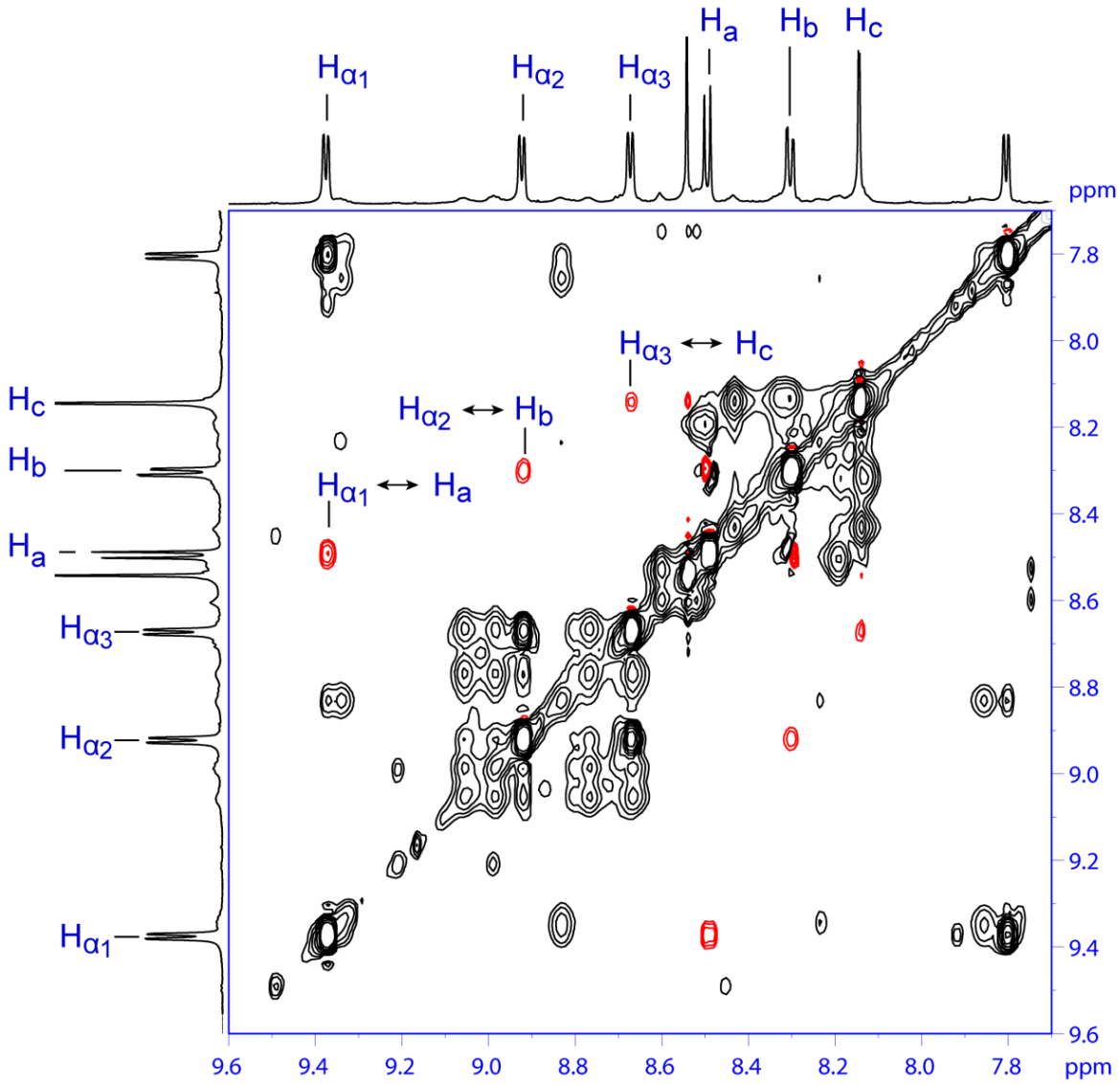


Fig. S10. A region of the NOESY (600 MHz, CD_3CN, 298 K) spectrum of *trans*–**3**•$4PF_6$. Note the strong black peaks are phased positive (chemical exchange peaks for the dynamic equilibrium between the Fo8 and another conformation) and the red peaks are phased negative and correspond to positive nOe's (correlation of the Figure-of-Eight). This region of the spectrum shows the through-space correlations of the bipyridinium protons α to the nitrogen and the xylylene protons. These key correlations allow for the assignment of the protons in this region.

Furthermore, correlations between the methylene protons and the bipyridinium α protons are observed along with the correlations between the methylene protons and xylylene protons (Figure S11). These nOes allow for the assignment of the methylene protons with respect to their orientation — i.e., H_A is pointed towards the same side of the bipyridinium unit as $H_{\alpha 1}$ and H_a.

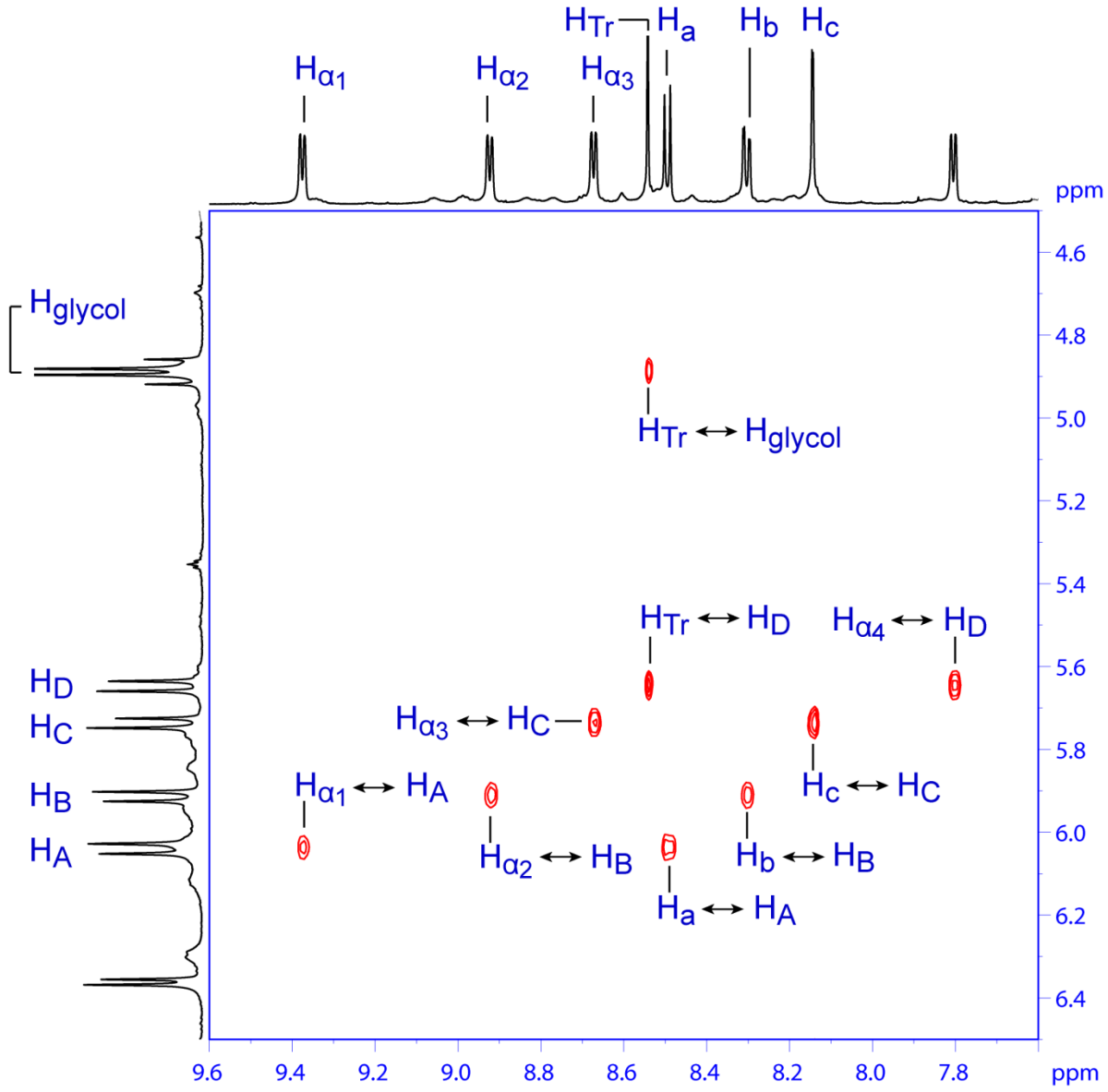


Fig. S11. A region of the NOESY (600 MHz, CD_3CN, 298 K) spectrum of *trans*–**3**•4PF_6.Through-space correlations of the bipyridinium protons α to the nitrogen and the methylene protons are observed. Furthermore, xylylene protons have through-space correlations with the methylene protons. By observing these correlations, parts of the structure can be elucidated.

Finally, the bipyridinium protons β to the nitrogen correlate to each other so that each bipyridinium unit may be fully assigned as the final portion of the assignment (Figure S12) — i.e., $H_{β1}$ is on the same bipyridinium unit as $H_{β3}$. The through-space correlation of $H_{β1}$ with $H_{β3}$ can only be assigned to the C_i symmetric *trans* constitution. Using all of the observed nOes, we can assign *trans*–**3**•4PF_6 fully as noted in Figure S5.

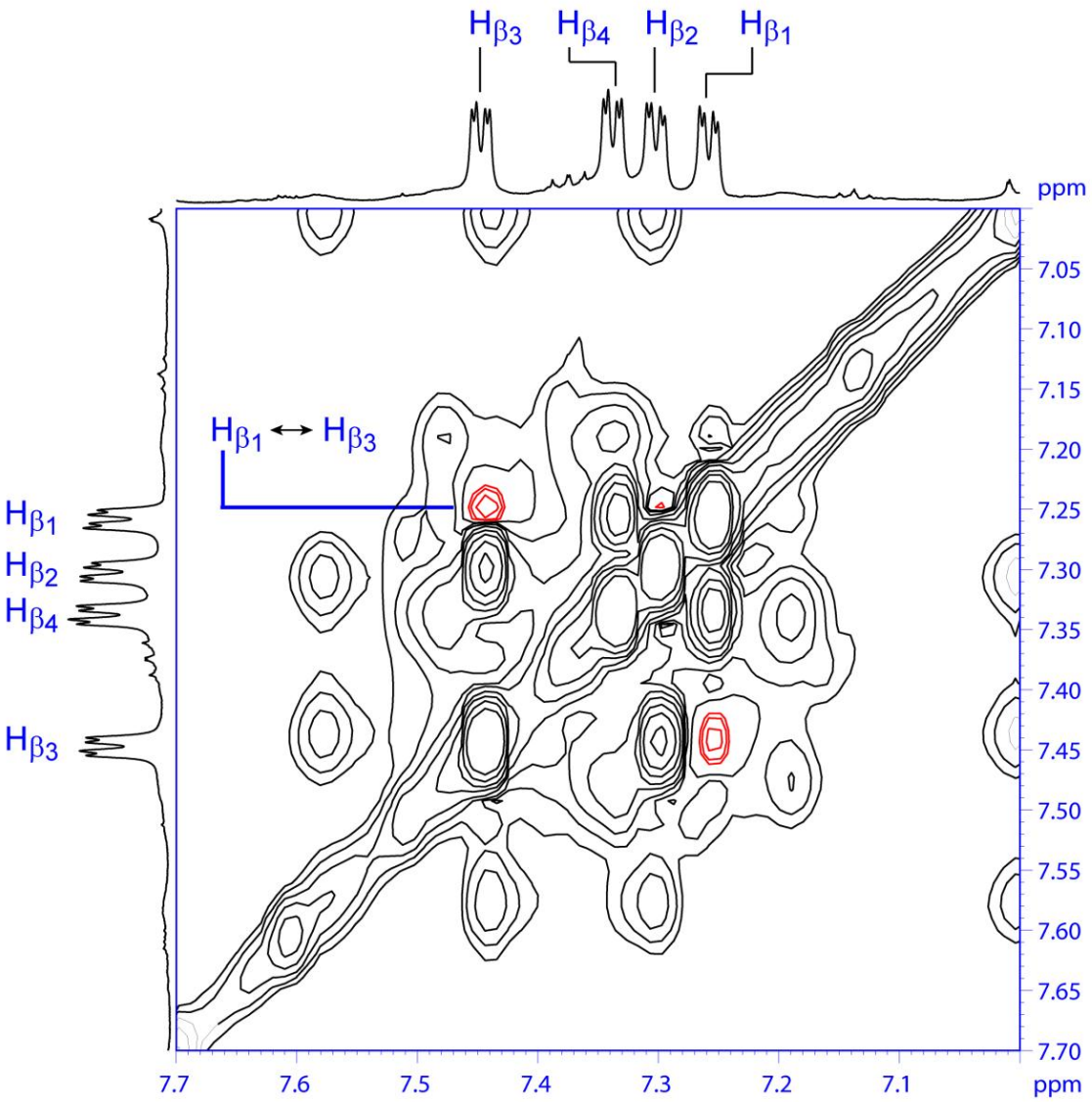


Fig. S12. A region of the NOESY (600 MHz, CD_3CN, 298 K) spectrum of *trans*–**3**•4PF_6. Note the key nOe signals (red; negative peaks) represent the orientation of the bipyridinium protons β to the nitrogen with respect to each other.

For *cis*–**3**•4PF_6, we also observe similar nOes as with the *trans* isomer; however, the correlations follow the symmetry as described for the *cis* isomer. Each bipyridinium proton α to a nitrogen has a through-space correlation with a xylylene proton (Figure S13). The correlations for each methylene proton with their respective bipyridinium α protons and xylylene protons are observed (Figure S14) so that each methylene may be assigned with respect to its orientation. Thus, the assignment of *cis*–**3**•4PF_6 is as shown in Figure S5.

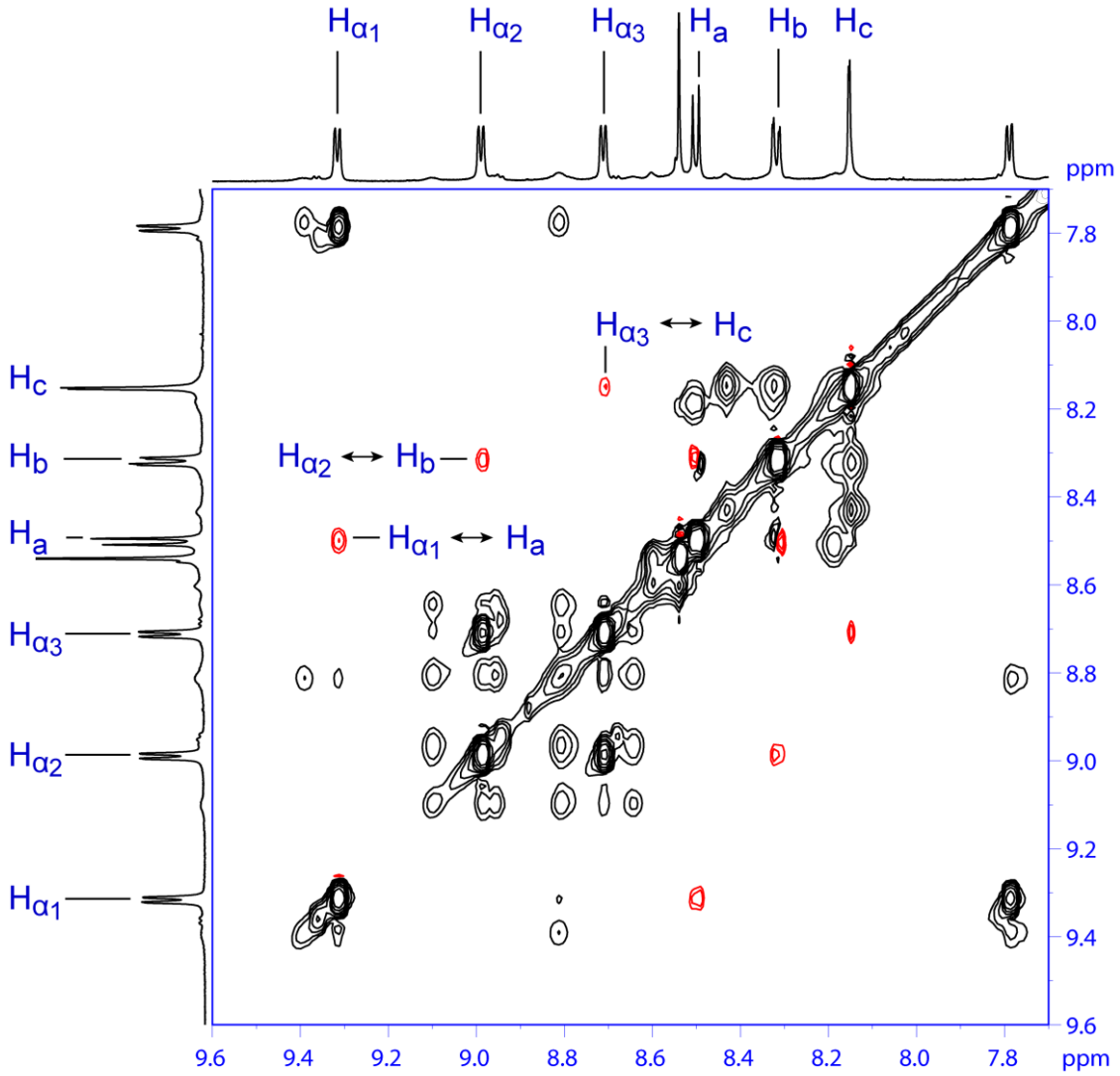


Fig. S13. A region of the NOESY (600 MHz, CD_3CN, 298 K) spectrum of *cis*–**3**•4PF_6. Note the black peaks are phased positive (chemical exchange peaks between the major and minor species) and the red peaks are phased negative (positive through-space nOe's of the Figure-of-Eight). The shown region of the spectrum shows the through-space correlations of the bipyridinium protons α to the nitrogen and the xylylene protons. These key correlations allow for the assignment of the protons in this region.

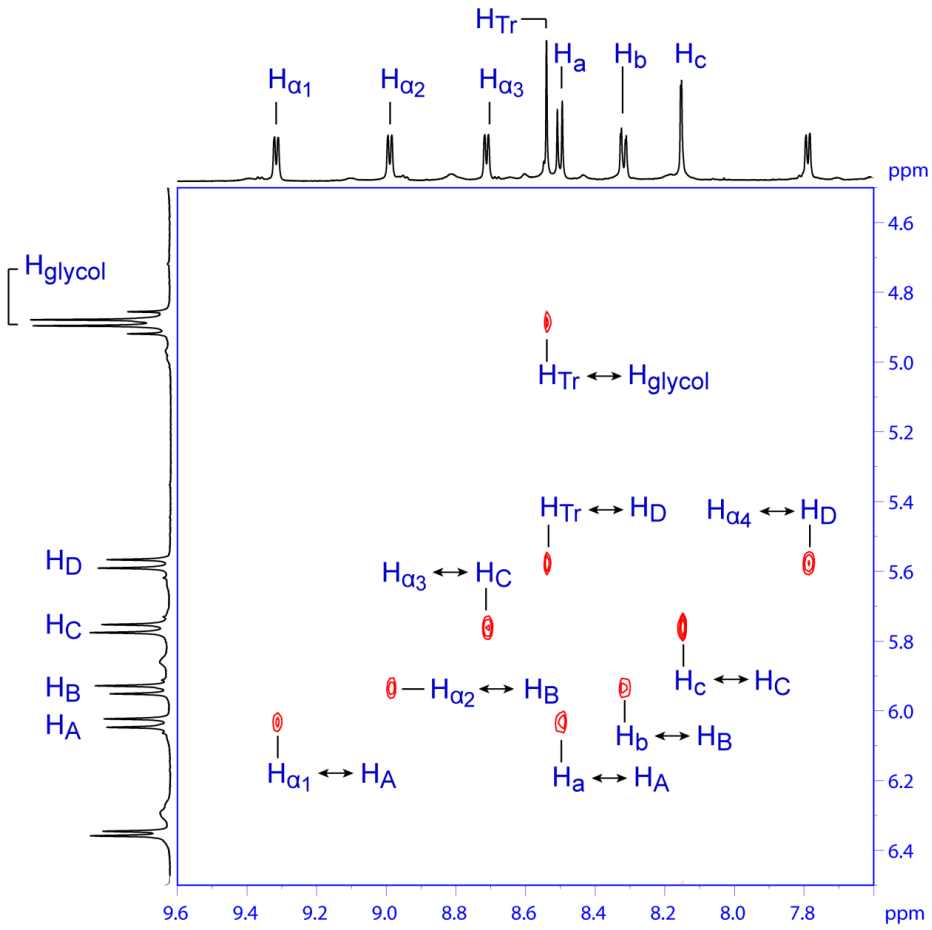


Fig. S14. A region of the NOESY (600 MHz, CD_3CN, 298 K) spectrum of *cis*–**3**•4PF_6.Through-space correlations of the bipyridinium protons α to the nitrogen and the methylene protons are observed. Furthermore, xylylene protons have through-space correlations with the methylene protons. By observing these correlations, parts of the structure can be elucidated.

To summarize this data, both isomers of **3**•4PF_6 have been fully assigned using 2D COSY and NOESY experiments with the key correlation shown in Figure S12.

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