Phosphine Oxide Functional Group Based Three-Station Molecular Shuttle

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SUPPORTING INFORMATION

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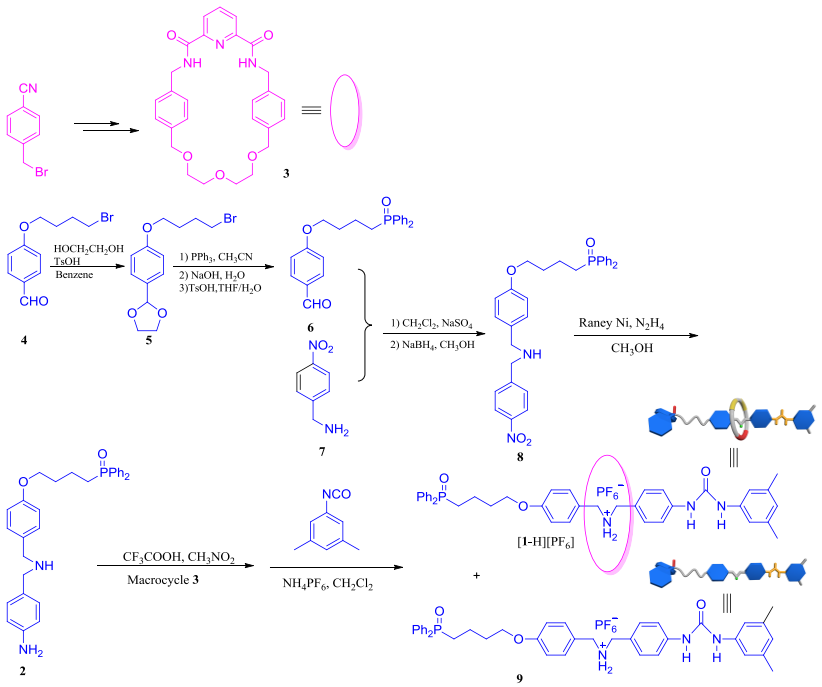
1. Materials and methods

All reactions were performed in open atmosphere unless otherwise stated. All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous CH_2Cl_2 and CH_3CN were obtained by distillation from CaH_2 under N_2 atmosphere. Melting points (M.p.) were determined using a Focus X-4 apparatus and were not corrected. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz or 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. 2D COSY and 2D ROESY experiments were performed on a Bruker DPX 400 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

2. Experimental procedures



Scheme S1. Synthesis of [2]rotaxane [**1**-H][PF_6]

2-(4-(4-bromobutoxy)phenyl)-1,3-dioxolane 5: *p*-Toluenesulfonic acid monohydrate (0.10 g, 0.5 mmol) as a catalyst was added to a solution of **4** (2.57 g, 10 mmol) and ethylene glycol (6.20 g, 100 mmol) in benzene (60 mL) and then the mixture was refluxed for 24 h in an apparatus fitted with a Dean-Stark condenser under N_2. The reaction mixture was subsequently poured into aqueous sodium hydrogen carbonate solution, extracted with diethyl ether (2 × 100 mL) and the combined extracts were washed with aqueous sodium hydrogen carbonate solution and water, dried over $MgSO_4$ and concentrated under vacuum to give dioxolane **5** as yellow oil. The crude dioxolane was used directly for the next step without further purification.

4-(4-(diphenylphosphoryl)butoxy)benzaldehyde 6[S1]**:** A mixture of **5** (2.88 g, 9.6 mmol) and triphenylphosphine (2.51 g, 9.6 mmol) in anhydrous acetonitrile (60 mL) was heated at 80 ℃ for 24 h and then the solvent was evaporated under reduced pressure. Sodium hydroxide (1.92 g, 48 mmol) was added to the residue in water (30 mL) and the reaction mixture was refluxed for 12 h. 2 N HCl was added to acidify the solution until pH = 2, and extracted with chloroform (3 × 50 mL). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated under vacuum. *p*-Toluenesulfonic acid monohydrate (0.10 g, 0.5 mmol) as a catalyst was added to a solution of the residue in THF (30 mL) and water (30 mL) then the mixture was refluxed for 12 h and cooled to RT. After THF was removed under reduced pressure, saturated sodium hydrogen carbonate solution (30 mL) was added. The mixture was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH, 100:1) to afford **6** as a white solid (2.72 g, 72% yield in two steps). M.p. 86-87 ℃; The ^1H & ^{13}C NMR spectra of **6** are shown in Fig. S3-S4. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H, C*H*O), 7.81 (d, 2H, *J* = 8.8 Hz, Ar*H*), 7.77-7.72 (m, 4H, Ar*H*), 7.55-7.44 (m, 6H, Ar*H*), 6.93 (d, 2H, *J* = 8.7 Hz, Ar*H*), 4.03 (t, 2H, *J* = 6.0 Hz, OCH_2), 2.38-2.31 (m, 2H, O=PCH_2), 1.98-1.91 (m, 2H, CH_2), 1.90-1.79 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 163.8, 132.8 (d, ^1J (C, P) = 98 Hz, Ar*C*P), 131.8, 131.7 (d, ^4J (C, P) = 2 Hz, Ar*C*H), 130.6 (d, ^3J (C, P) = 9 Hz, Ar*C*H), 129.7, 128.6 (d, ^2J (C, P) = 12 Hz, Ar*C*H), 114.6, 67.4, 29.9 (d, ^2J (C, P) = 14 Hz, O=PCH$_2$*C*H$_2$), 29.2 (d, ^1J (C, P) = 72 Hz, O=P*C*H$_2$), 18.3 (d, ^3J (C, P) = 3 Hz, O=P CH$_2$CH$_2$*C*H$_2$); ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.2; HR-MS (ESI): m/z calcd for [**6**+Na]$^+$ $C_{23}H_{23}NaO_3P^+$, 401.1283, found

401.1311.

Nitro compound 8: A mixture of **6** (0.88 g, 2.3 mmol), Na_2SO_4 (3.27 g, 23 mmol) and (4-nitrophenyl)methanamine **7** (0.35 g, 2.3 mmol) in anhydrous dichloromethane (25 mL) was stirred at RT for 24 h. Then Na_2SO_4 was filtered off. The solvent was evaporated under reduced pressure. $NaBH_4$ (0.27 g, 7.0 mmol) was added to the residue in methanol (30 mL) under ice-bath. Then the ice-bath was removed and the mixture was stirred for 5 h. After removing most of the solvent, 50 mL H_2O was added to quench the reaction. The mixture was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH, 100:1) to afford **8** as yellow oil (1.03 g, 87%). The ^1H & ^{13}C NMR spectra of **8** are shown in Fig. S5-S6. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, 2H, *J* = 8.7 Hz, Ar*H*), 7.76-7.70 (m, 4H, Ar*H*), 7.53 (d, 2H, *J* = 8.8 Hz, Ar*H*), 7.52-7.44 (m, 6H, Ar*H*), 7.22 (d, 2H, *J* = 8.6 Hz, Ar*H*), 6.80 (d, 2H, *J* = 8.6 Hz, Ar*H*), 3.93 (t, 2H, *J* = 6.0 Hz, OCH_2), 3.89 (s, 2H, CH_2), 3.75 (s, 2H, CH_2), 2.37-2.31 (m, 2H, O=PCH_2), 2.05 (br, 1H, N*H*), 1.91-1.78 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 148.3, 147.0, 133.0 (d, ^1J (C, P) = 98 Hz, Ar*C*P), 131.9, 131.7 (d, ^4J(C,P) = 2 Hz, Ar*C*H), 130.8 (d, ^3J(C,P) = 9 Hz, Ar*C*H), 129.3, 128.7, 128.7 (d, ^2J(C,P) = 11 Hz, Ar*C*H), 123.6, 114.5, 67.1, 56.2, 52.6, 30.3 (d, ^2J(C,P) = 14 Hz, O=PCH$_2$*C*H$_2$), 29.4 (d, ^1J(C,P) = 72 Hz, O=P*C*H$_2$), 18.5 (d, ^3J(C,P) = 3 Hz, O=PCH$_2$CH$_2$*C*H$_2$); ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.6; HR-MS (ESI): m/z calcd for [**8**+Na]$^+$ $C_{30}H_{31}N_2NaO_4P^+$, 537.1919, found 537.1923.

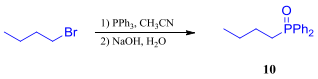
Amine 2: A mixture of **8** (1.03 g, 2 mmol) and Raney Ni (Cat.) in methanol was heated to reflux at 80 ℃. Then $N_2H_4 \cdot H_2O$ (1.8 mL, 40 mmol) was added. The reaction was refluxed for 6 h. Then the solution was cooled to RT. The catalyst was filtered off. The solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL), and the organic phase was washed with water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH, 20:1) to afford **2** as a yellow solid (0.87 g, 90%). M.p. 56-58 ℃; The ^1H & ^{13}C NMR spectra of **2** are shown in Fig. S7-S8. ^1H NMR (400 MHz, CD_3CN): δ = 7.70-7.67 (m, 4H, Ar*H*), 7.54-7.47 (m, 6H, Ar*H*), 7.27 (d, 2H, *J* = 8.6 Hz, Ar*H*), 7.10 (d, 2H, *J* = 8.4 Hz, Ar*H*), 6.78 (d, 2H, *J* = 8.6 Hz, Ar*H*), 6.58 (d, 2H, *J* = 8.4 Hz, Ar*H*),

4.13 (br, 3H, N*H*), 3.90 (t, 2H, *J* = 6.3 Hz, OCH_2), 3.70 (s, 2H, CH_2), 3.65 (s, 2H, CH_2), 2.38-2.29 (m, 2H, O=PCH_2), 1.86-1.73 (m, 2H, CH_2), 1.66-1.55 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 146.5, 132.8 (d, ^1J (C, P) = 98 Hz, Ar*C*P), 131.8 (d, ^4J (C, P) = 3 Hz, Ar*C*H), 130.7 (d, ^3J (C, P) = 9 Hz, Ar*C*H), 130.5, 130.4, 128.7 (d, ^2J (C, P) = 12 Hz, Ar*C*H), 127.8, 125.0, 115.0, 114.5, 67.0, 50.8 , 50.4, 30.2 (d, ^2J (C,P) = 14 Hz, O=PCH$_2$*C*H$_2$), 29.3 (d, ^1J (C, P) = 72 Hz, O=P*C*H$_2$), 18.4 (d, ^3J (C, P) = 4 Hz, O=PCH$_2$CH$_2$*C*H$_2$); ^{31}P NMR (160 MHz, $CDCl_3$) : δ = 32.9; HR-MS (ESI): m/z calcd for [**2**+H]$^+$ $C_{30}H_{34}N_2O_2P^+$, 485.2358, found 485.2471.

[**1**-H][PF_6][S2]: Trifluoroacetic (37 μL, 0.5 mmol) was added to a solution of amine **2** (0.24g, 0.5 mmol) and macrocycle **3**[S3, S4] (0.24g, 0.5 mmol) in anhydrous CH_3NO_2. The mixture was stirred for 1 h. After 3,5-dimethylphenyl isocyanate (87 μL, 0.6 mmol) was added, the resulting mixture was stirred at RT for 48 h and then the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL). Then saturated NH_4PF_6 solution (10 mL) was added. The mixture was stirred for 1 h and then water (20 mL) was added. The aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH, 20:1) to afford [2]Rotaxane [**1**-H][PF_6] as a white solid and dumbbell-shaped salt **9** as a yellow solid. [**1**-H][PF_6] (75 mg, 12%). M.p. 185-187 ℃; The ^{1}H & ^{13}C NMR spectra of [**1**-H][PF_6] are shown in Fig. S9-S10. ^{1}H NMR (400 MHz, CD_3CN/$CDCl_3$ (*v*/*v* = 1:1)) : δ = 9.01 (br, 2H, CON*H*), 8.43 (d, 2H, *J* = 7.8 Hz, Ar*H*), 8.18 (t, 1H, *J* = 7.8 Hz, ArH), 7.76-7.71 (m, 4H, Ar*H*), 7.56-7.49 (m, 7H, Ar*H* and NHCON*H*), 7.35 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.27 (br, 1H, NHCON*H*), 7.21 (br, 2H, NH_2), 7.08 (d, 4H, *J* = 7.8 Hz, Ar*H*), 7.04 (s, 2H, ArH), 6.96 (d, 2H, *J* = 8.9 Hz, ArH), 6.94 (d, 2H, J = 9.3 Hz, Ar*H*), 6.82 (d, 4H, *J* = 7.9 Hz, Ar*H*), 6.67 (s, 1H, ArH), 6.65 (d, 2H, *J* = 8.7 Hz, Ar*H*), 4.73-4.58 (m, 4H, ArCH_2), 4.24-4.19 (m, 4H, ArCH_2), 3.91 (t, 2H, *J* = 6.3 Hz, OCH_2), 3.65-3.57 (m, 4H, OCH_2), 3.31-3.21 (m, 4H, OCH_2), 2.50 (br, 4H, ArCH_2), 2.44 -2.37 (m, 2H, POCH_2), 2.38-2.29 (m, 2H, O=PCH_2), 2.25 (s, 6H, ArCH_3), 1.91-1.86 (m, 2H, CH_2), 1.81-1.72 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 159.0, 153.6, 149.4, 141.4, 140.8, 138.9, 138.7, 134.4, 132.6 (d, ^1J (C, P) = 99 Hz, Ar*C*P), 132.2, 130.9 (d, ^3J (C, P) = 9, Ar*C*H), 129.4, 129.2, 129.0 (d, ^2J (C, P) = 12 Hz, Ar*C*H), 128.5, 127.8, 125.5, 124.9, 124.2, 123.4, 118.3, 117.4, 114.2, 74.5, 70.5, 69.6, 67.2, 51.5, 50.5, 42.4, 30.4 (d, ^2J (C, P)

= 14, $POCH_2CH_2$), 29.4 (d, ^1J (C, P) = 71, O=PCH_2), 21.5, 18.6 (d, ^3J (C, P) = 2, $POCH_2CH_2CH_2$); ^{31}P NMR (160 MHz, CD_3CN): δ = 30.6; LR-ESI-MS: calcd. for [**1**+H]$^+$ $C_{66}H_{72}N_6O_8P^+$: 1107.51, found *m*/*z* = 1107.35; HR-MS (ESI): m/z calcd for [**1**+H]$^+$ $C_{66}H_{72}N_6O_8P^+$, 1107.5144, found 1107.5152; [**1**+Na]$^+$ $C_{66}H_{71}N_6NaO_8P^+$, 1129.4963, found 1129.4975.

9: 116 mg, 30%. M.p. 152-155 ℃; The ^{1}H & ^{13}C NMR spectra of [**2**-H][PF_6] are shown in Fig. S11-S12. ^{1}H NMR (400 MHz, $CD_3CN/CDCl_3$ (*v*/*v* = 1:1)) : δ = 7.76 (br, 1H, NHCON*H*), 7.70-7.66 (m, 4H, Ar*H*), 7.51-7.48 (m, 7H, Ar*H*), 7.40 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.29 (d, 2H, *J* = 8.6 Hz, Ar*H*), 7.24 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.04 (s, 2H, Ar*H*), 6.81 (d, 2H, *J* = 8.5 Hz, Ar*H*), 6.68 (s, 2H, Ar*H*), 4.09 (br, 4H, ArCH_2), 3.92 (t, 2H, *J* = 5.9 Hz, OCH_2) 2.41-2.30 (m, 2H, O=PCH_2), 2.26 (s, 6H, ArCH_3), 1.89-1.82 (m, 2H, CH_2), 1.71-1.61 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CD_3CN/CDCl_3$ (*v*/*v* = 1:1)): δ =160.7, 153.8, 141.8, 140.1, 139.5, 133.5, 133.2 (d, ^4J (C, P) = 2 Hz), 133.0 (d, ^1J (C, P) = 99 Hz), 132.7, 131.9, 131.6 (d, ^3J (C, P) = 10 Hz), 129.9 (d, ^2J (C, P) = 12 Hz), 125.4, 123.9, 119.7, 117.9, 115.6, 68.1, 51.8, 51.6, 30.7 (d, ^2J (C, P) = 15 Hz), 28.9 (d, ^1J (C, P) = 72 Hz), 21.5, 19.1 (d, ^3J (C, P) = 4 Hz); ^{31}P NMR (160 MHz, CD_3CN): δ = 34.0; LR-ESI-MS: calcd. for [**9**+H]$^+$ $C_{39}H_{43}N_3O_3P^+$ *m*/*z* 632.30, found 632.20; HR-MS (ESI): m/z calcd for [**9**+H]$^+$ $C_{39}H_{43}N_3O_3P^+$, 632.3037, found 632.3064; [**9**+Na]$^+$ $C_{39}H_{42}N_3NaO_3P^+$, 654.2856, found 654.2865.



10

Scheme S2. Synthesis of butyldiphenylphosphine oxide **10**

10[S1]**:** A mixture of 1-bromo-butane (1.37 g, 10.0 mmol) and triphenylphosphine (2.621 g, 10.0 mmol) in anhydrous acetonitrile (60 mL) was heated at 80 ℃ for 24 h and then the solution was cooled to RT. After solvent was evaporated under reduced pressure, sodium hydroxide (2.0 g, 50 mmol) was added to the residue in water (30 mL) and the reaction mixture was refluxed for 12 h. 2 N HCl was added to acidify the solution until pH = 2, and extracted with chloroform (3 × 50 mL). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH, 100:1) to afford **10** as a white solid (1.64 g, 64%). The ^{1}H NMR spectra of **10** are shown in Fig. S17. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.73 (m, 4H, Ar*H*), 7.52-7.49 (m, 6H, Ar*H*), 2.38-2.31 (m, 2H,

O=PCH_2), 1.63-1.61 (m, 2H, CH_2), 1.46-1.41 (m, 2H, CH_2), 0.90 (t, 3H, CH_3); ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.6; LR-ESI-MS: calcd. for [**10**+H]$^+$ $C_{16}H_{20}OP^+$: 259.12, found *m*/*z* = 259.10.

3. Dilution isotherm/Job plot for macrocycle 3 and phosphine oxide derivative 10 in $CDCl_3$

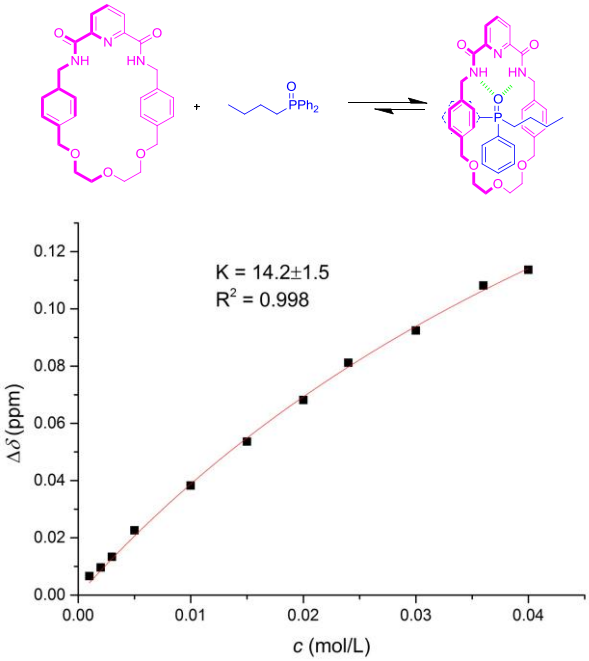


Fig. S1 The non-linear curve-fitting (NMR titrations) for the complexation of macrocycle **3** (host, 2 mM) with phosphine oxide derivative **10** (guest) in $CDCl_3$ at 298 K. The concentration of **10** was 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 18.0, 20.0, 24.0, 30.0, 36.0, 40.0 mM. Using the signal of free macrocycle **3** at δ 8.3489 as the reference.[S5]

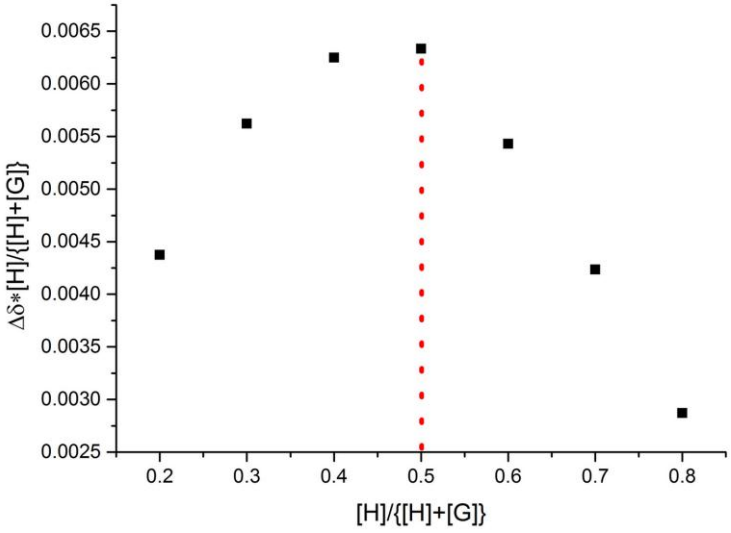


Fig. S2 The Job Plot (NMR titrations) for the complexation of macrocycle **3** (host) with phosphine oxide derivative **10** (guest) in $CDCl_3$ at 298 K. Using the signal of free macrocycle **3** at δ 7.8304 as the reference. ([H]+[G]) = 8 mM.[S5]

4. ^{1}H NMR and ^{13}C NMR for new compounds

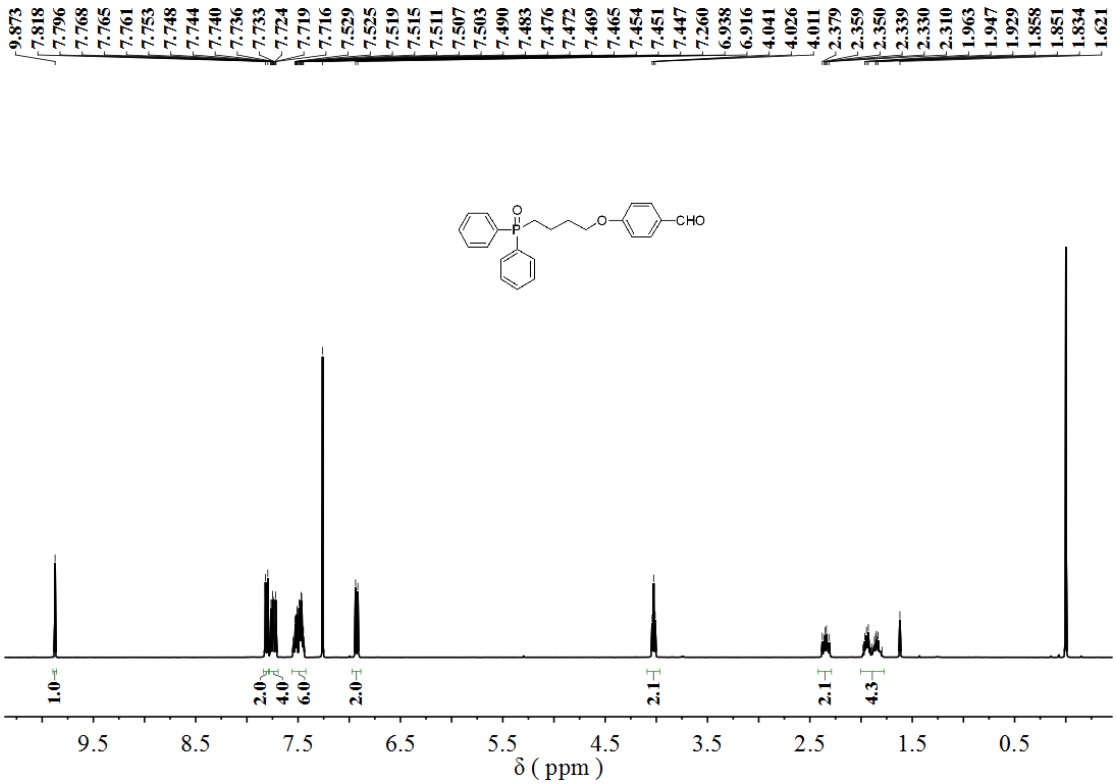


Fig. S3 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **6**.

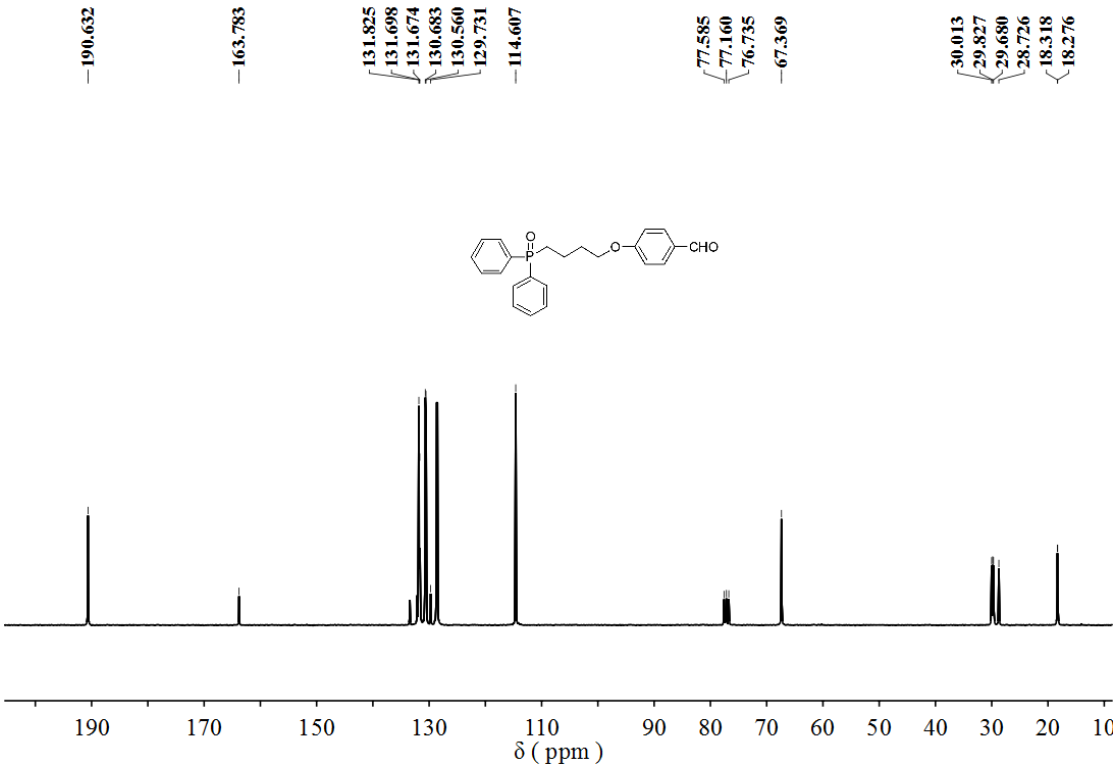


Fig. S4 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **6**.

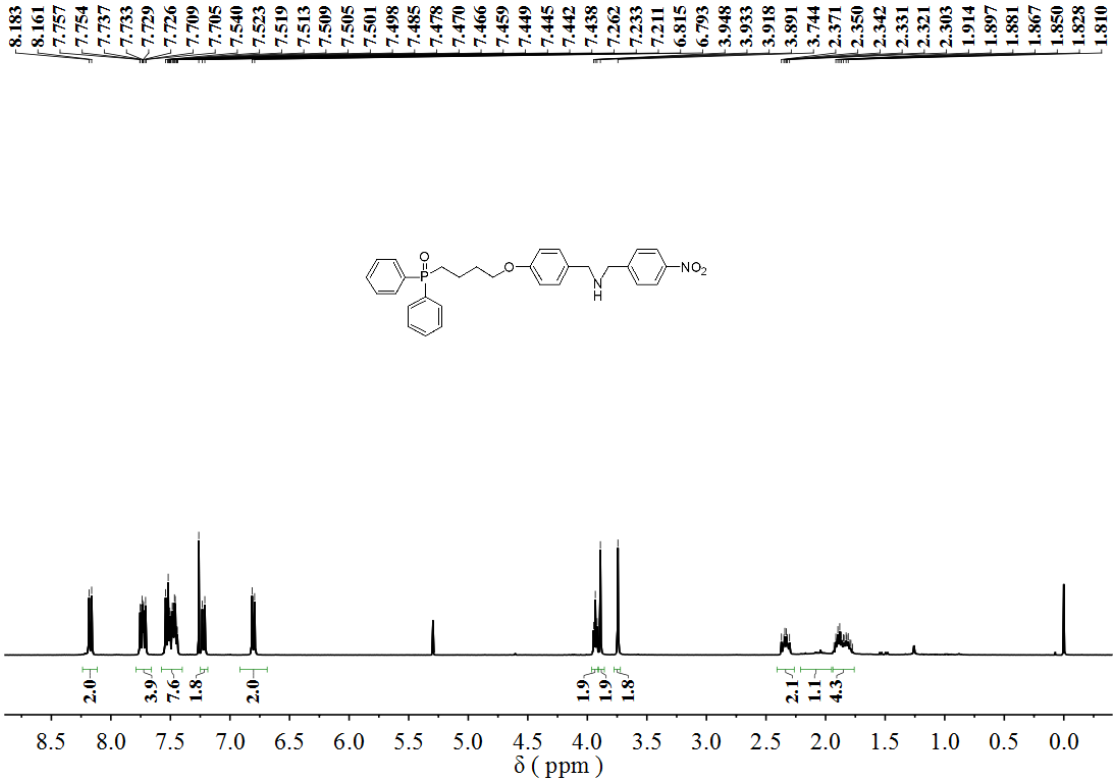


Fig. S5 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **8**.

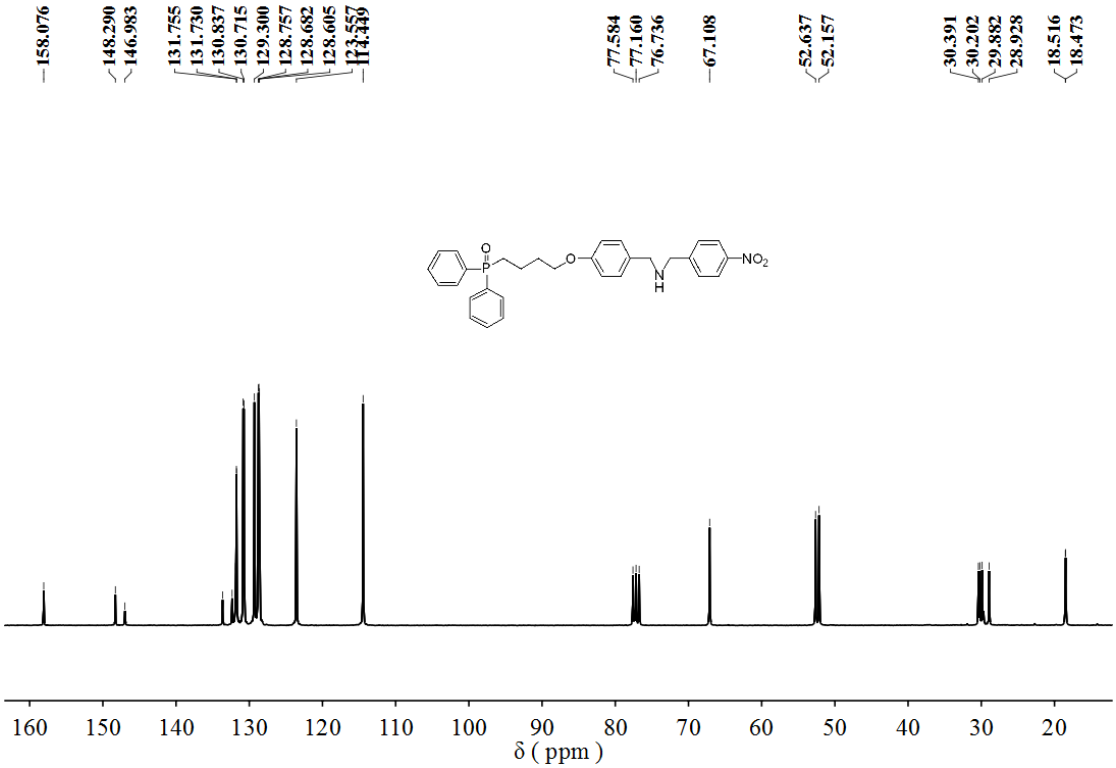


Fig. S6 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **8**.

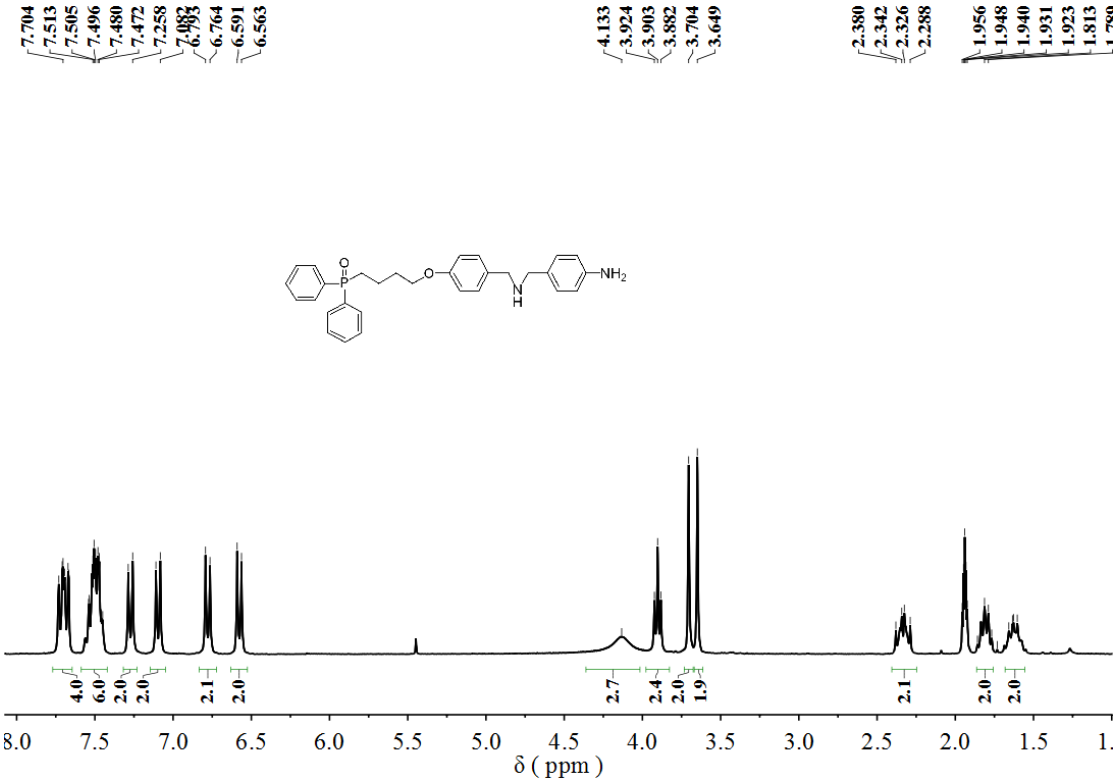


Fig. S7 ^{1}H NMR spectrum (CD_3CN, 400 MHz, 298 K) of **2**.

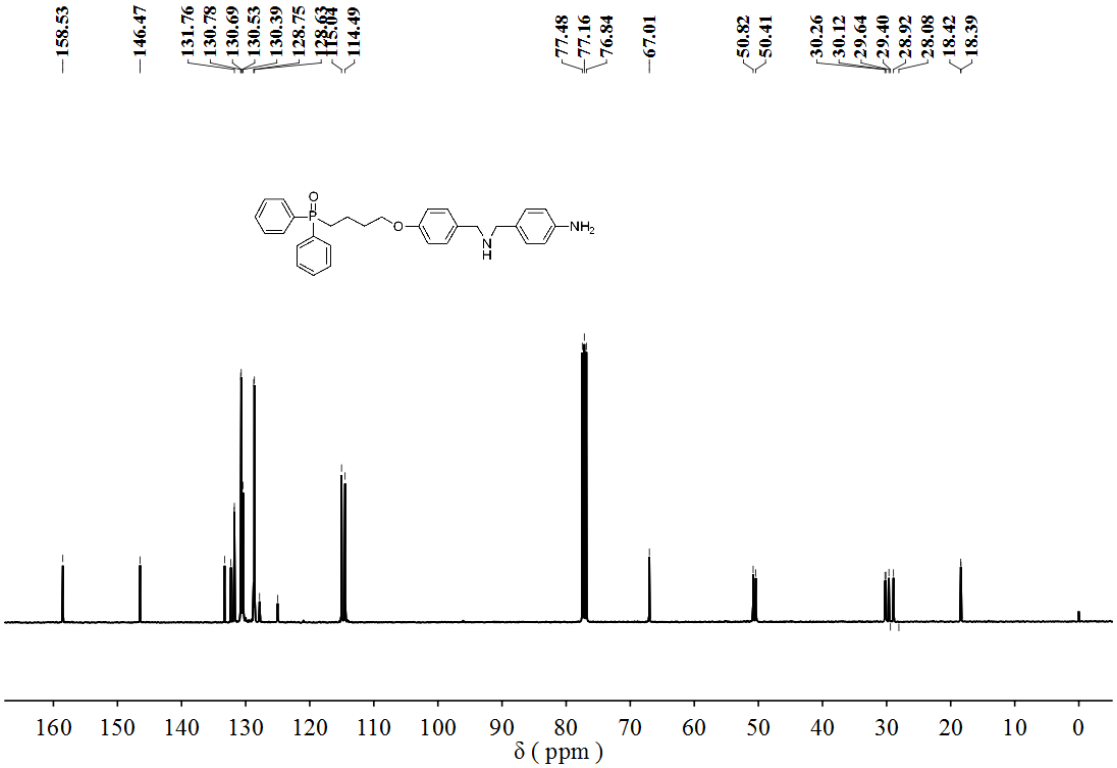


Fig. S8 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **2**.

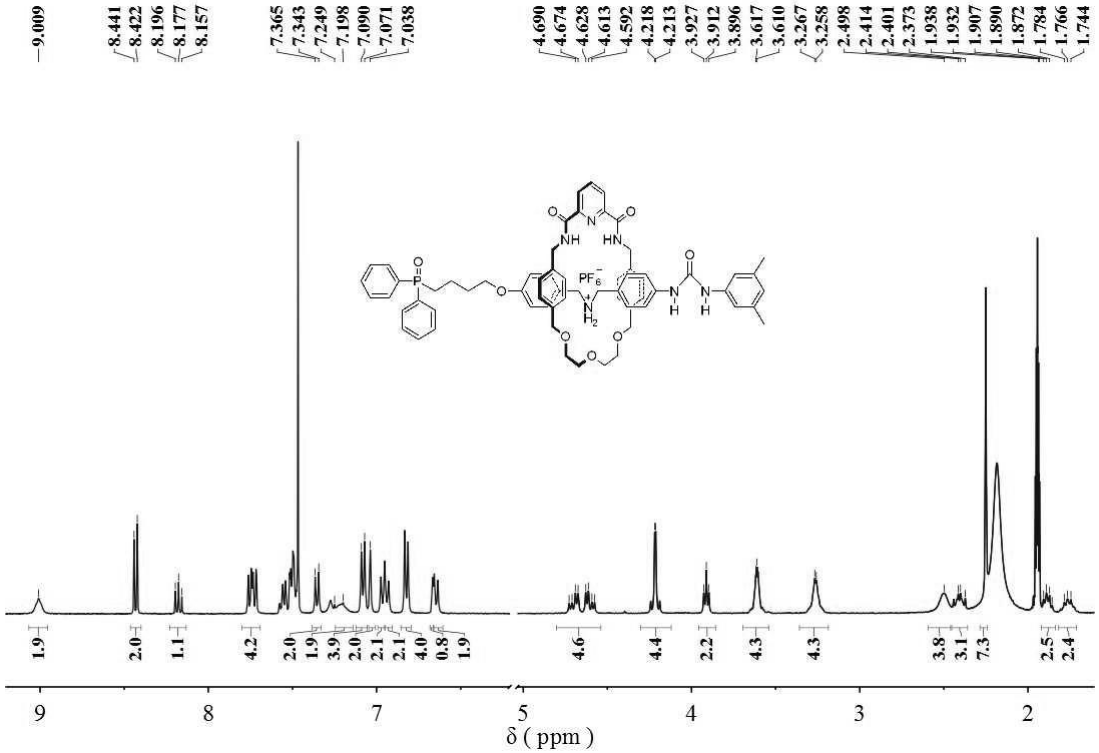


Fig. S9 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6].

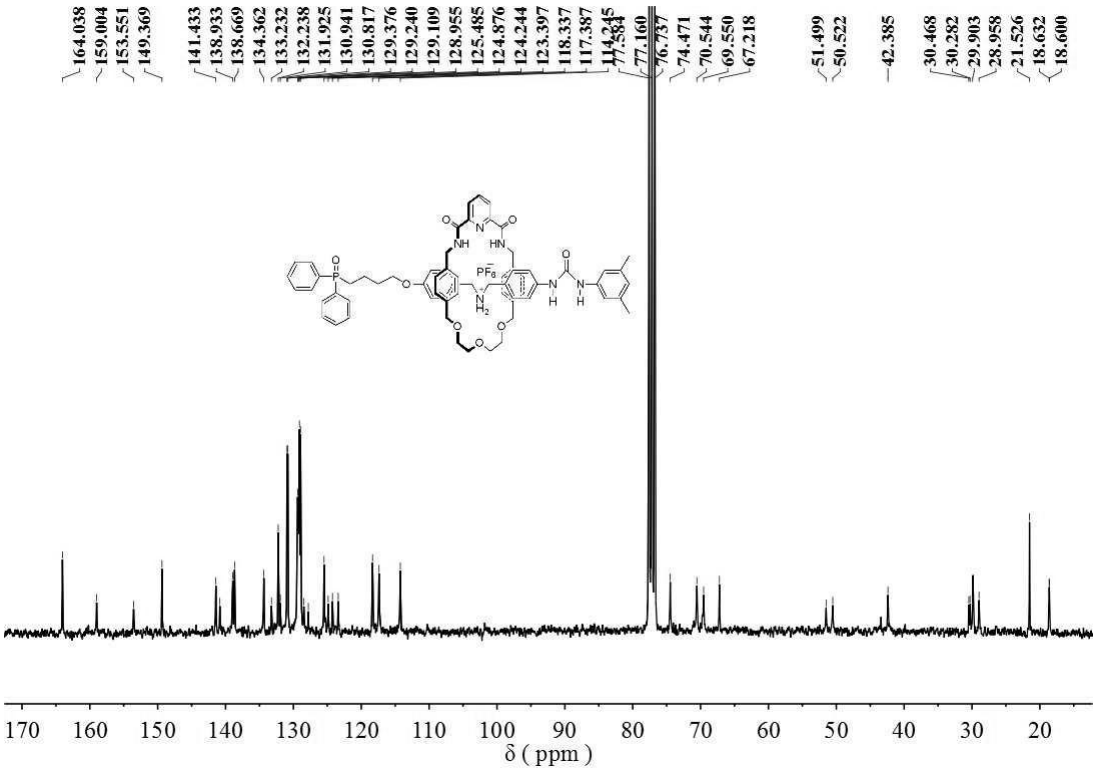


Fig. S10 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of [**1**-H][PF_6].

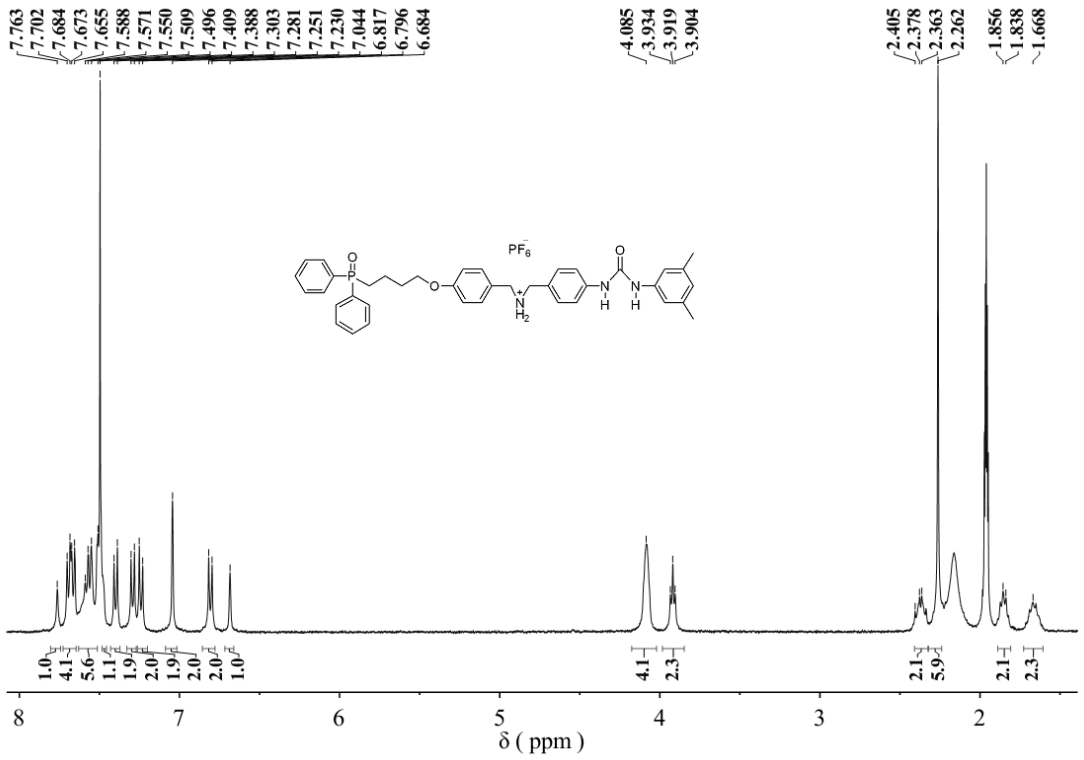


Fig. S11 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of **9**.

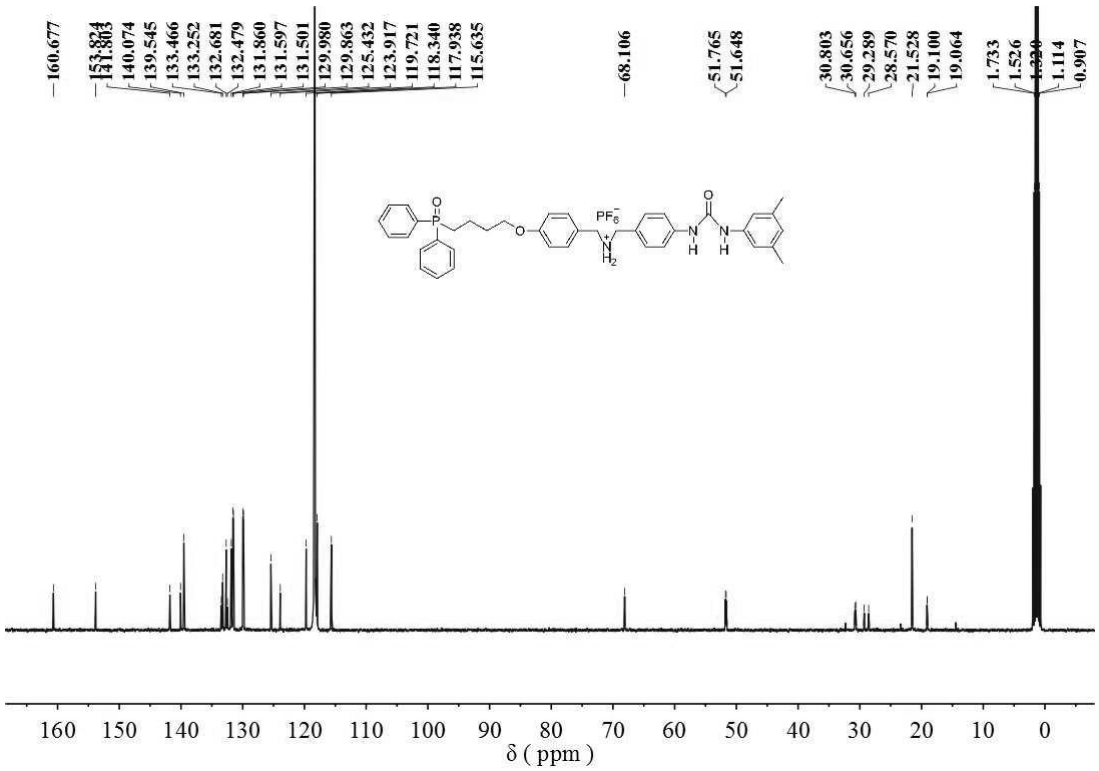


Fig. S12 ^{13}C NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 100 MHz, 298 K) of **9**.

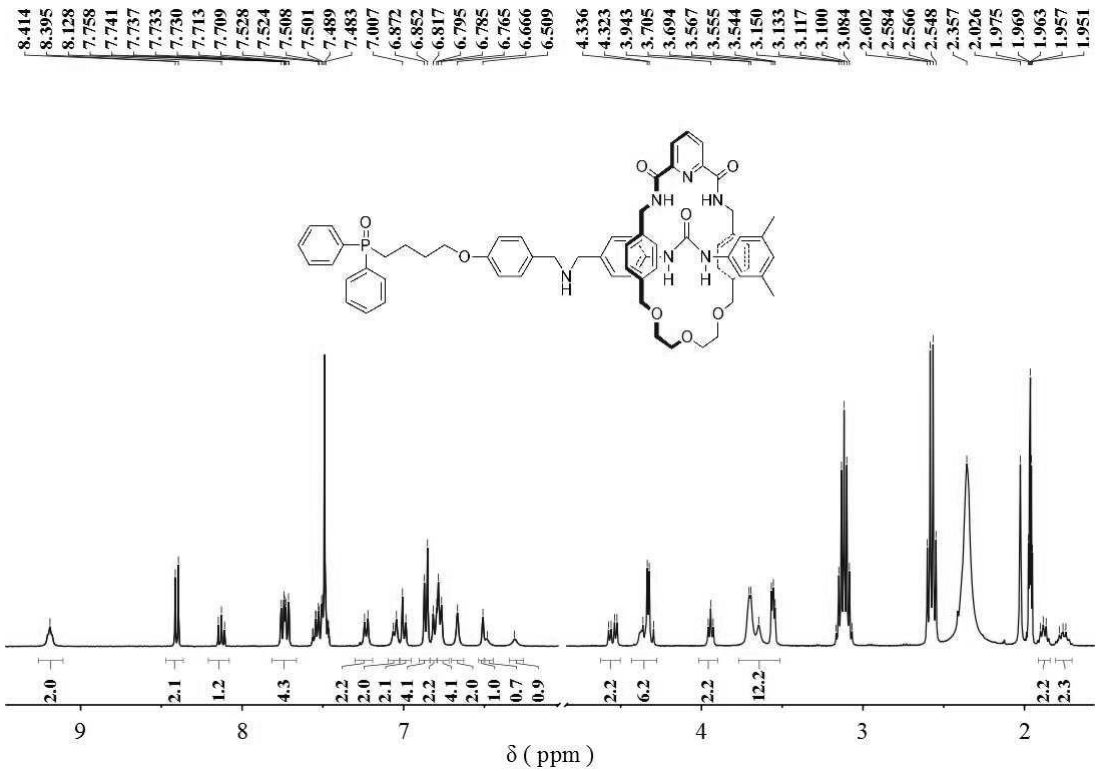


Fig. S13 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 1.5 equiv. of *i*Pr_2NEt.

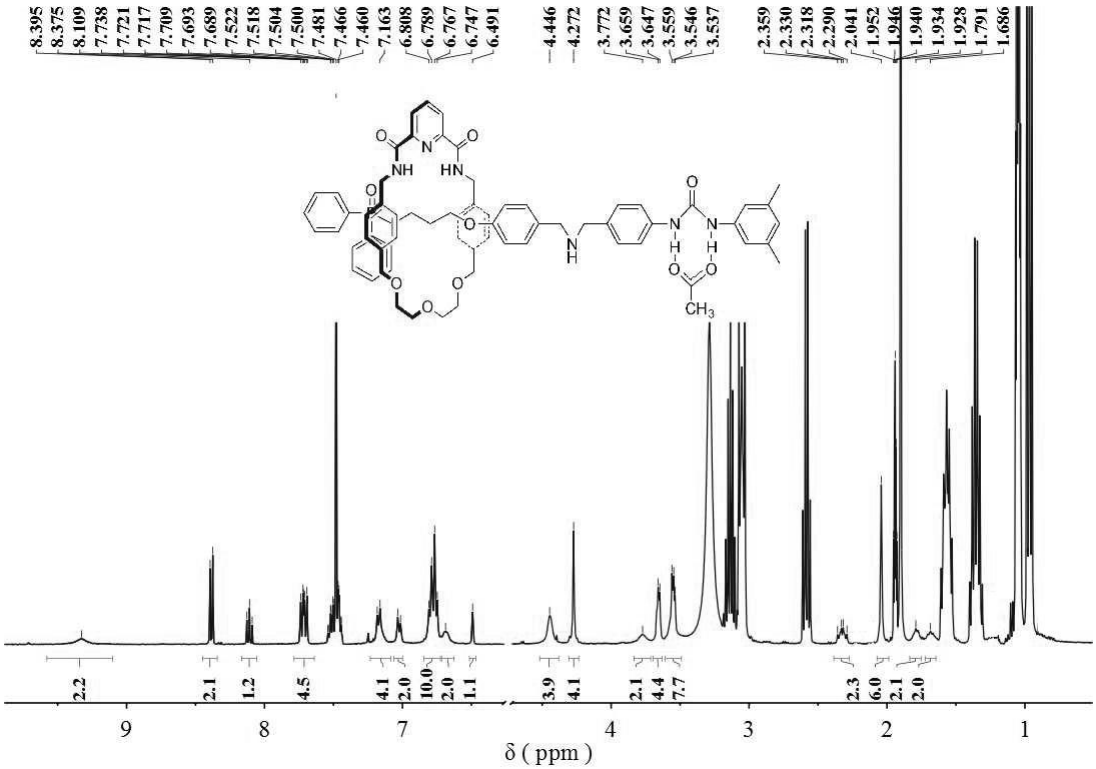


Fig. S14 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 1.5 equiv. of *i*Pr_2NEt and 2.0 equiv. of TBAA.

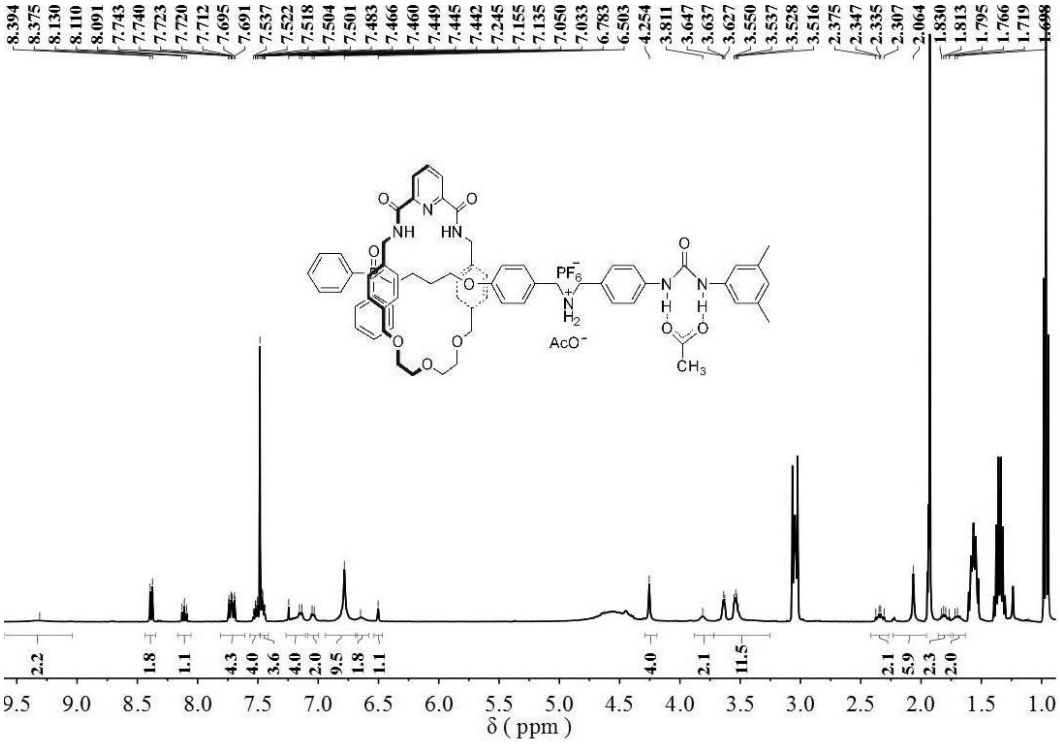


Fig. S15 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 3.0 equiv. of TBAA.

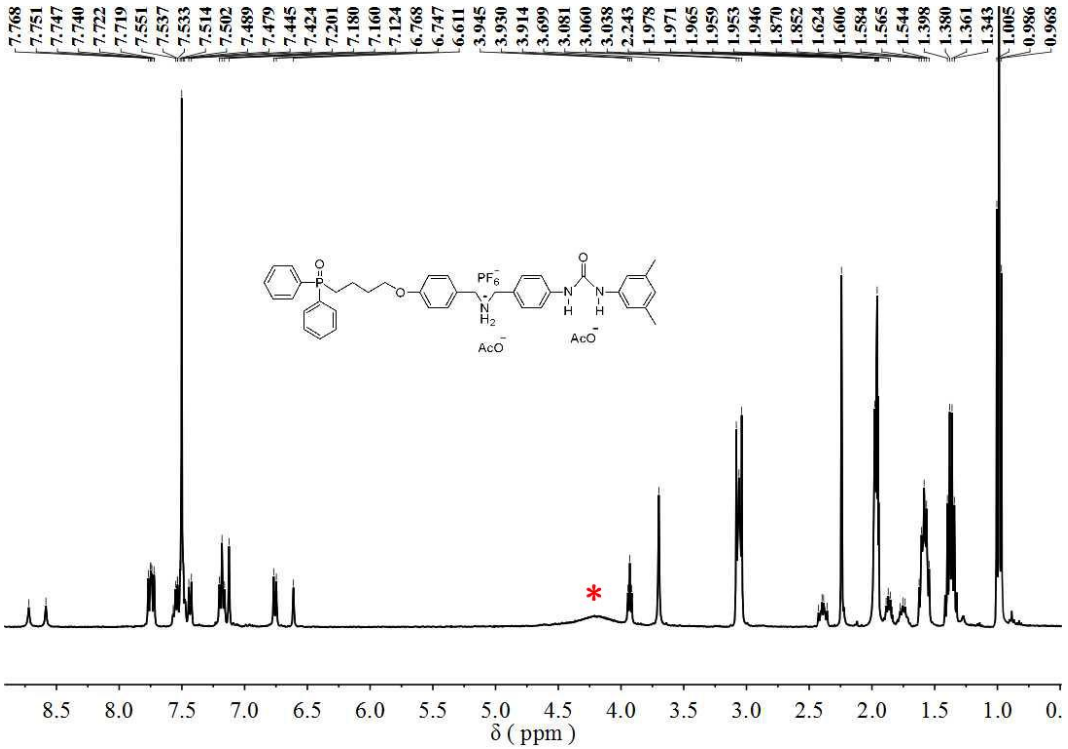


Fig. S16 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of **9** after the addition of 2.0 equiv. of TBAA (The peaks marked with * are ascribed to H_2O.).

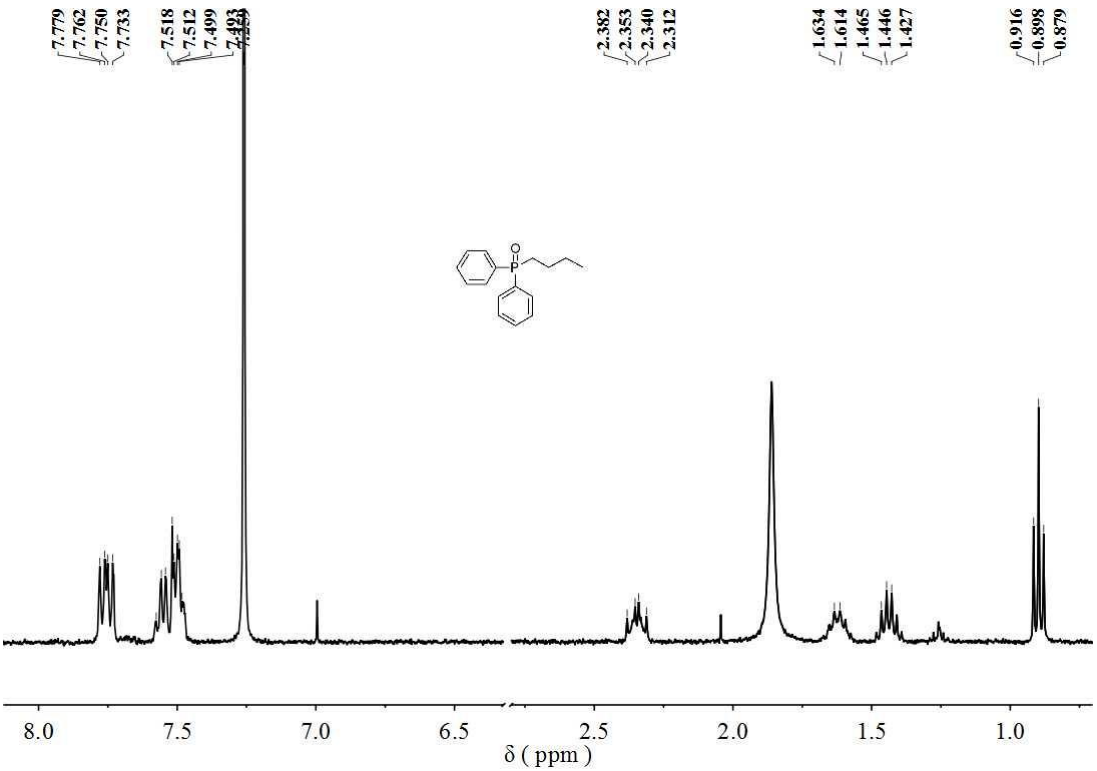


Fig. S17 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **10**.

5. ^{1}H NMR for the shuttling process

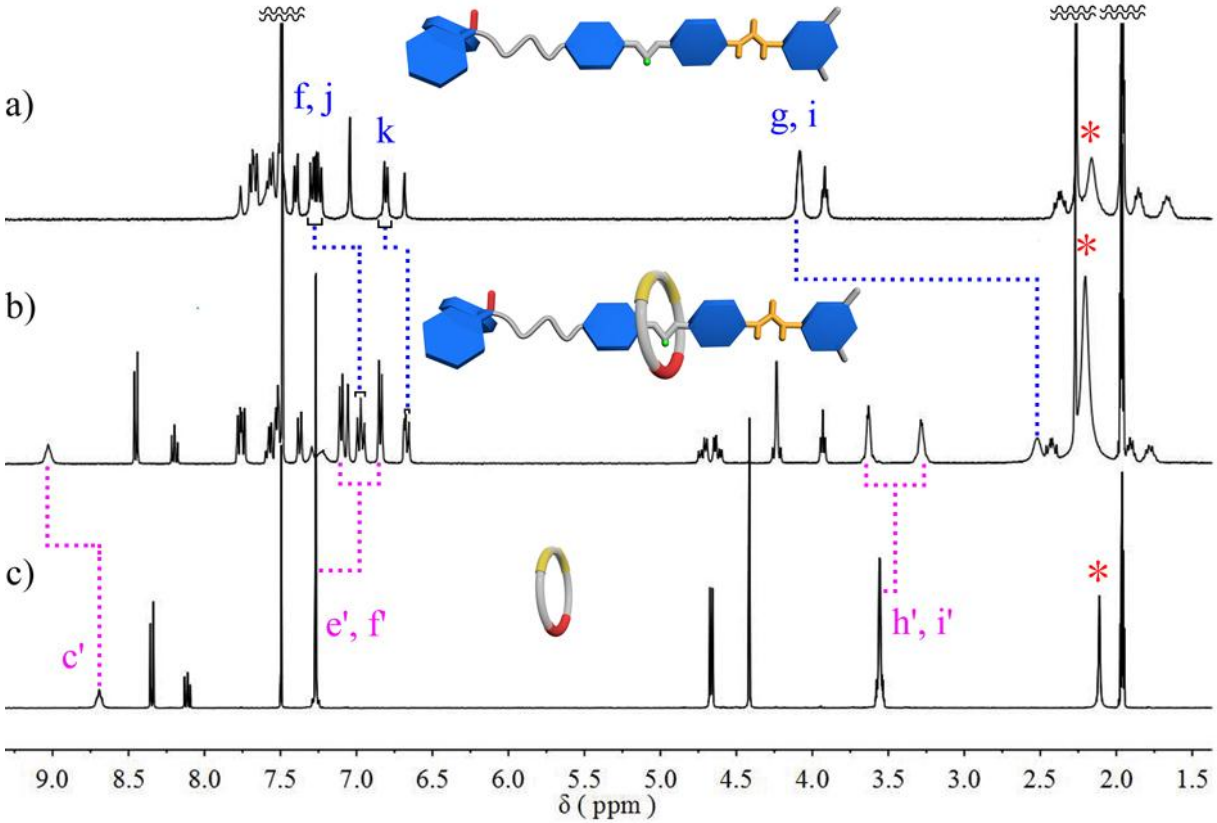


Fig. S18 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 298 K) of a) thread **9**, b) [2]rotaxane [**1**-H][PF_6], and c) macrocycle **3**. (The peaks marked with * are ascribed to H_2O.)

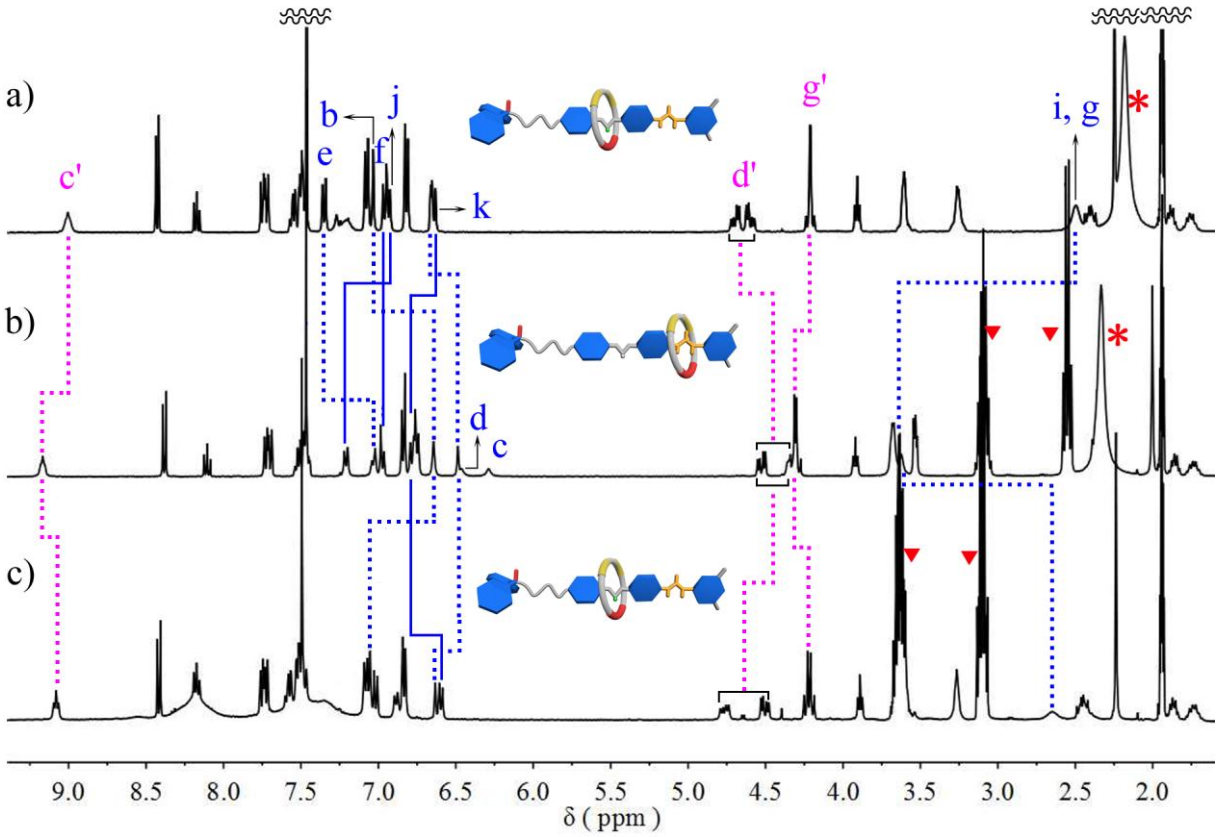


Fig. S19 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 298 K) of a) molecular shuttle [**1**-H][PF_6], b) the mixture obtained after adding *i*Pr_2NEt (1.5 equiv.) to the solution in a), c) the mixture obtained after adding TFA (2.0 equiv.) to the solution in b). (The peaks marked with * are ascribed to H_2O and the peaks marked with ▼ are ascribed to *i*Pr_2NEt).

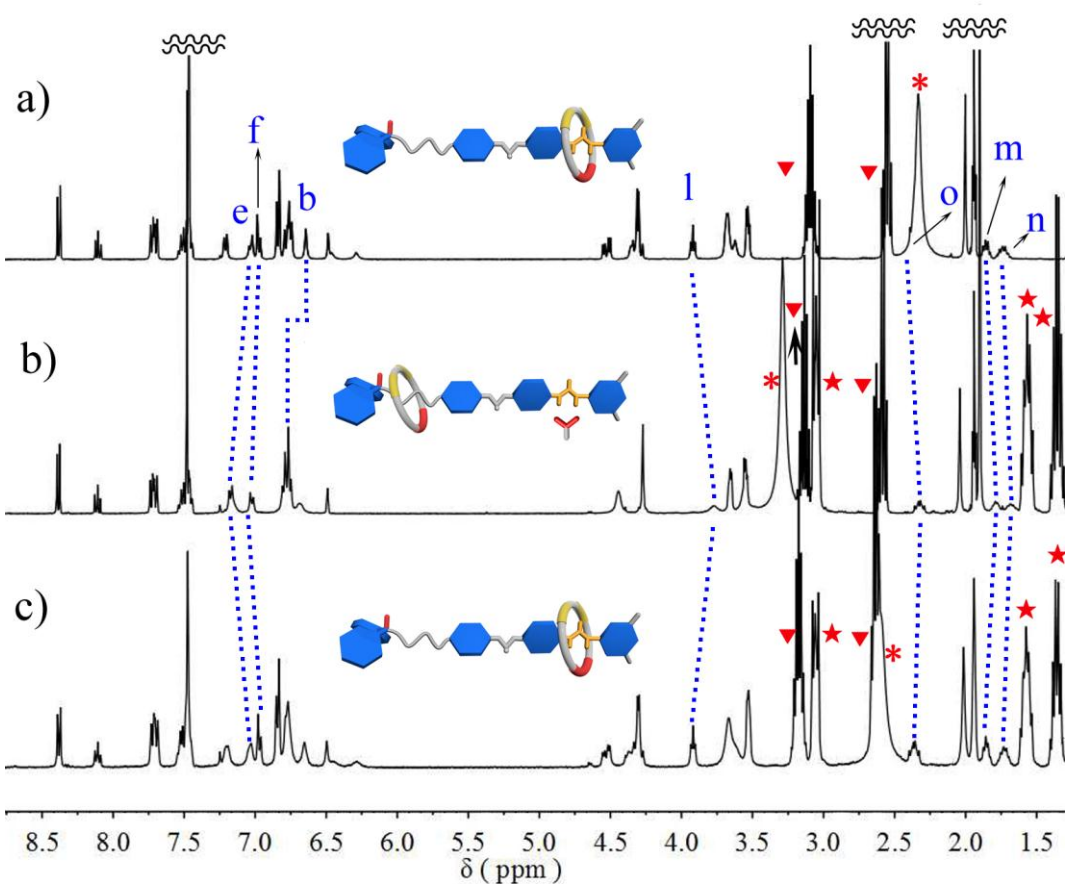


Fig. S20 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 298 K) of a) molecular shuttle [**1**-H][PF_6] after adding *i*Pr_2NEt (1.5 equiv.), b) the mixture obtained after adding TBAA (2.0 equiv.) to the solution in a), c) the mixture obtained after adding $NaClO_4$ (3.0 equiv.) to the solution in b). (The peaks marked with * are ascribed to H_2O, the peaks marked with ▼ are ascribed to *i*Pr_2NEt and the peaks marked with ★ are ascribed to TBAA)

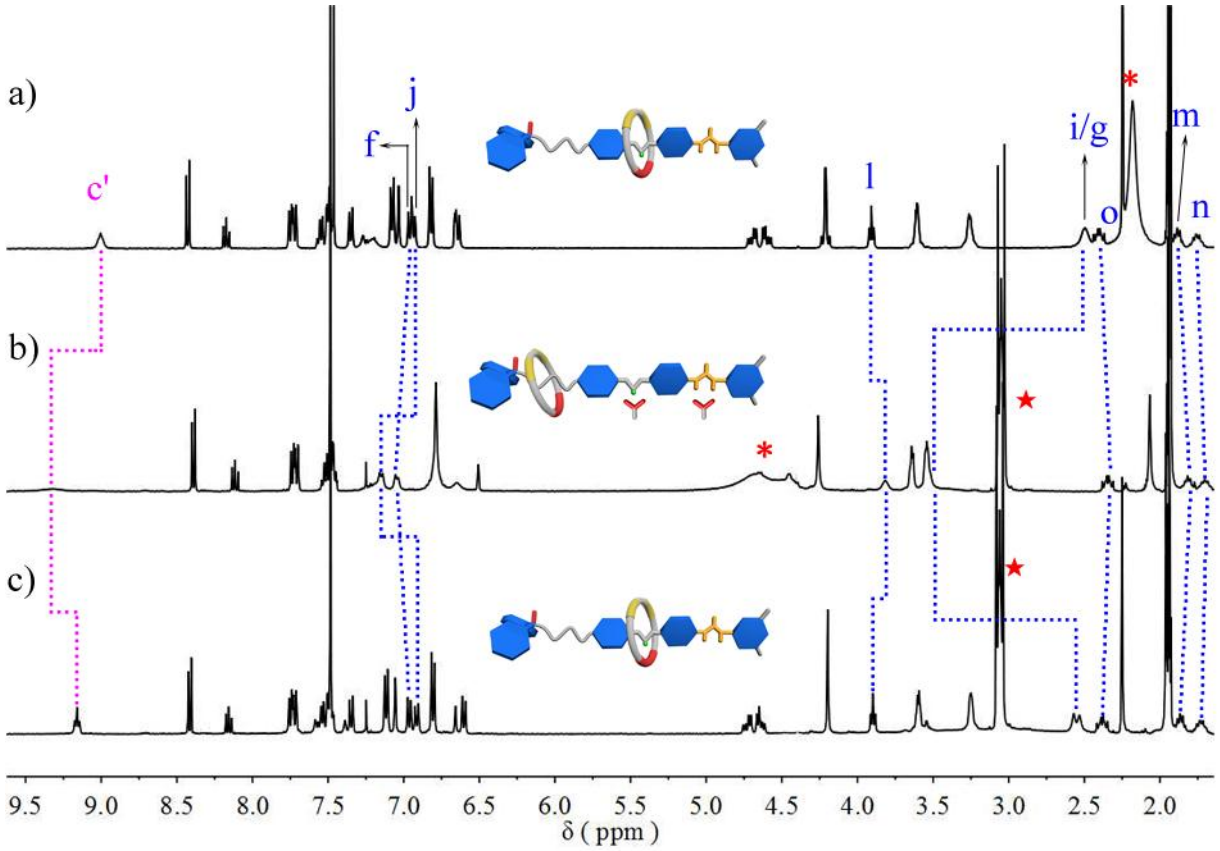


Fig. S21 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 298 K) of a) molecular shuttle [**1**-H][PF_6], b) the mixture obtained after adding TBAA (3.0 equiv.) to the solution in a), c) the mixture obtained after adding $NaClO_4$ (6.0 equiv.) to the solution in b). (The peaks marked with * are ascribed to H_2O and the peaks marked with ★ are ascribed to TBAA)

6. LR-ESI-MS of [1-H][PF_6] and 9

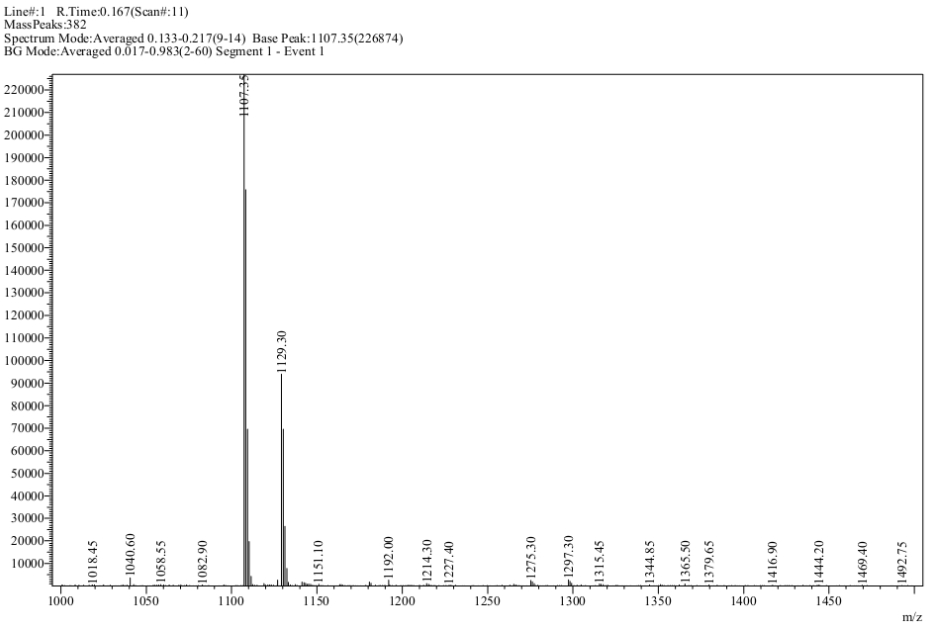


Fig. S22 LR-ESI-MS of [**1**-H][PF_6].

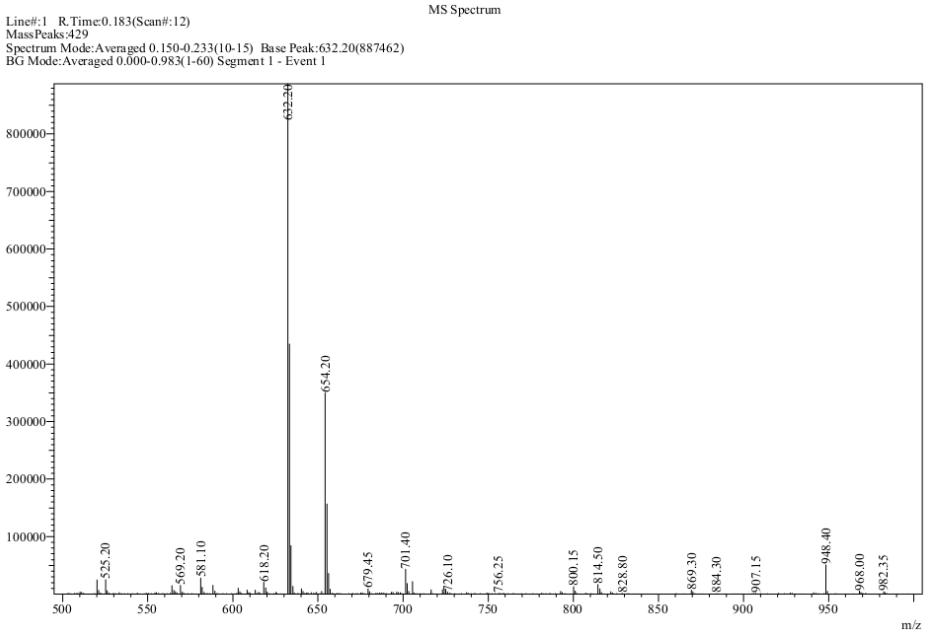


Fig. S23 LR-ESI-MS of **9**.

7. Partial 2D COSY and ROESY in different States

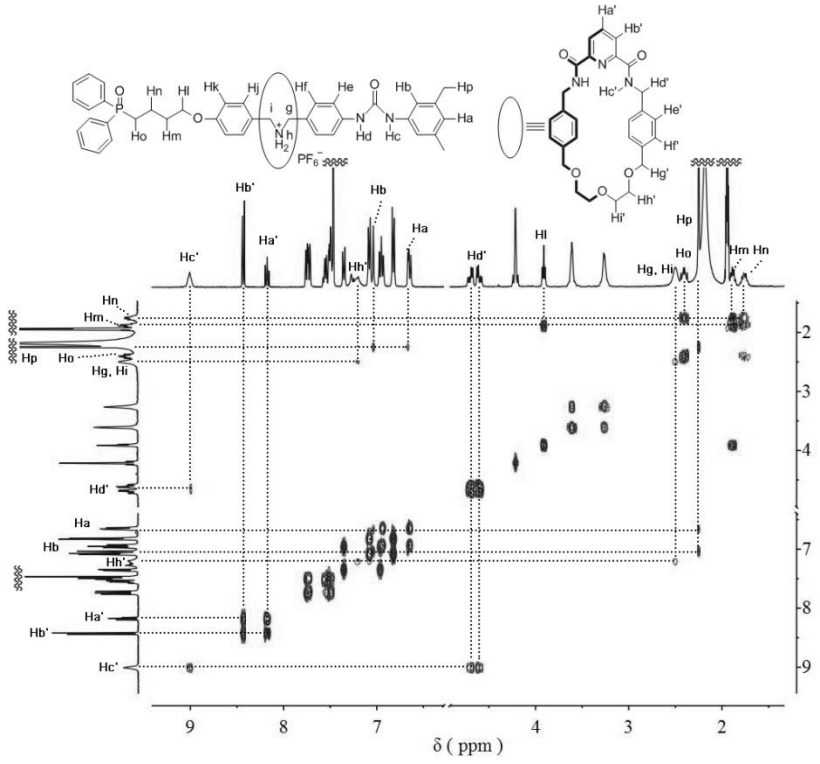


Fig. S24 Partial 2D COSY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6].

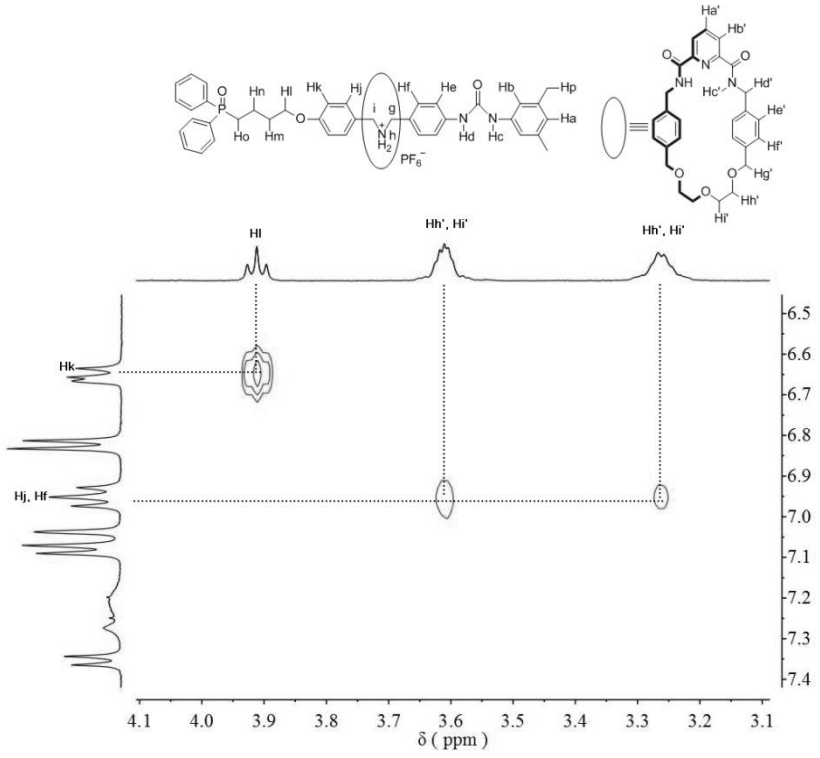


Fig. S25 Partial 2D ROESY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6].

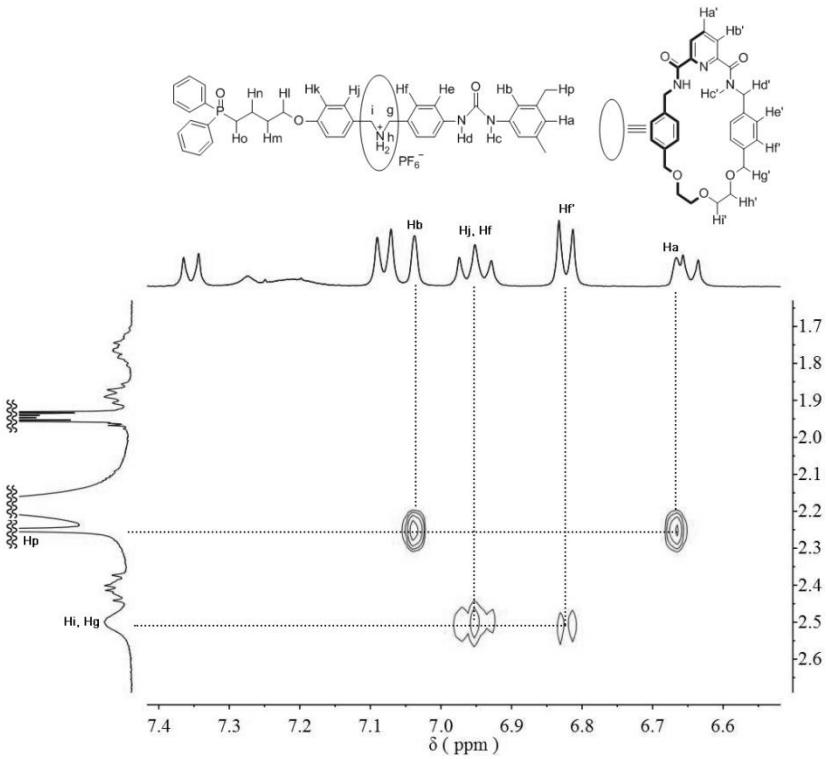


Fig. S26 Partial 2D ROESY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6].

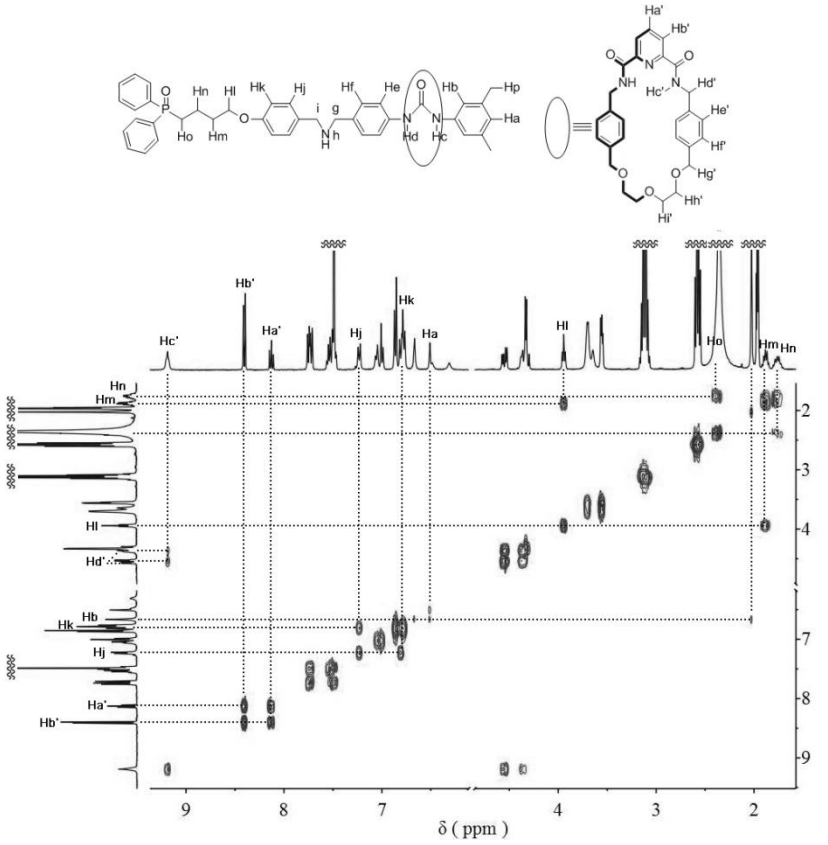


Fig. S27 Partial 2D COSY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 1.5 equiv. of *i*Pr_2NEt.

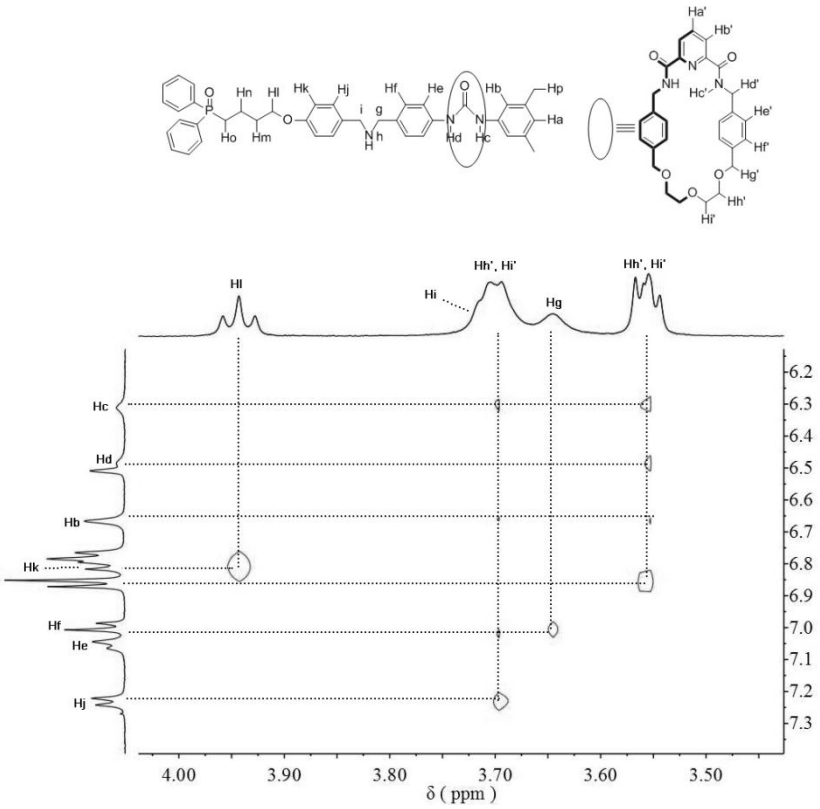


Fig. S28 Partial 2D ROESY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 1.5 equiv. of *i*Pr_2NEt.

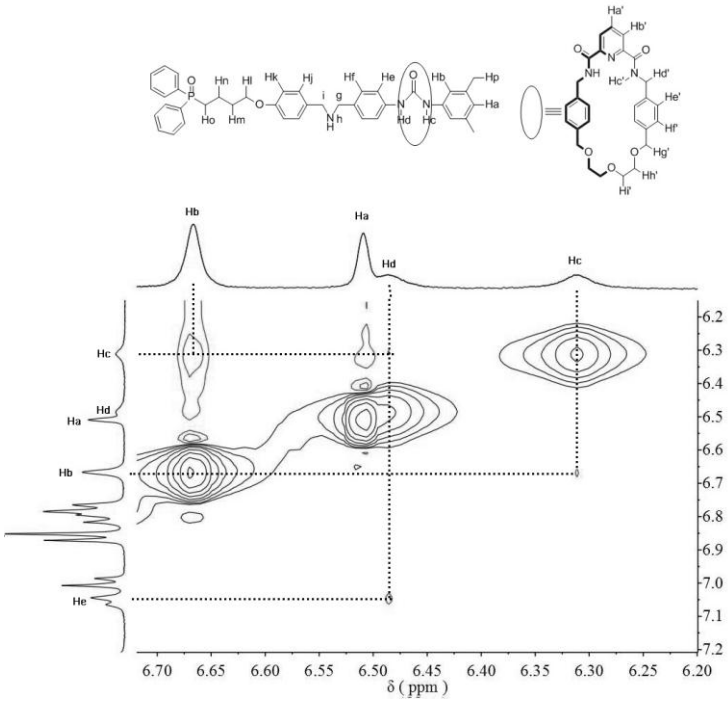


Fig. S29 Partial 2D ROESY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 1.5 equiv. of *i*Pr_2NEt.

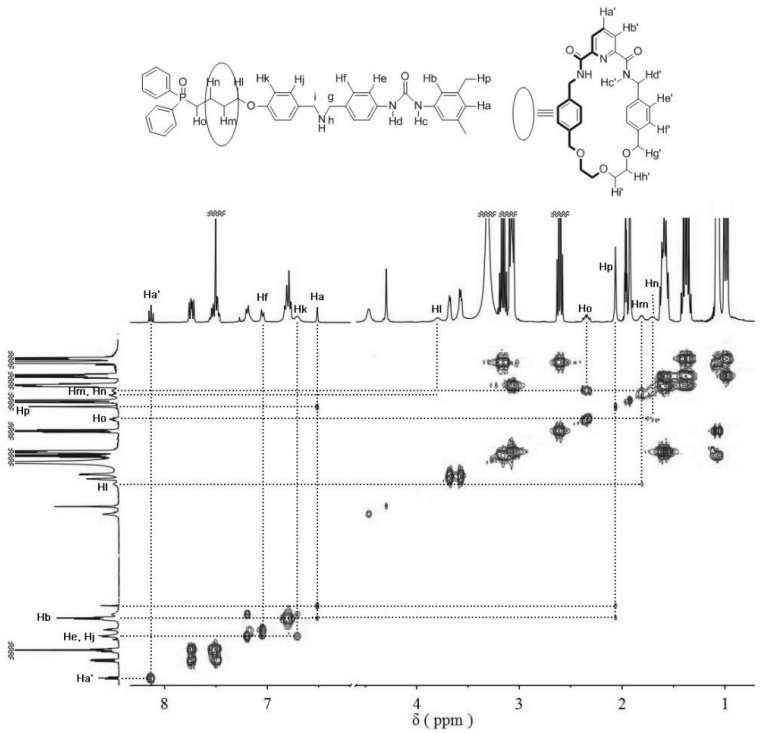


Fig. S30 Partial 2D COSY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 1.5 equiv. of *i*Pr_2NEt and 2.0 equiv. of TBAA.

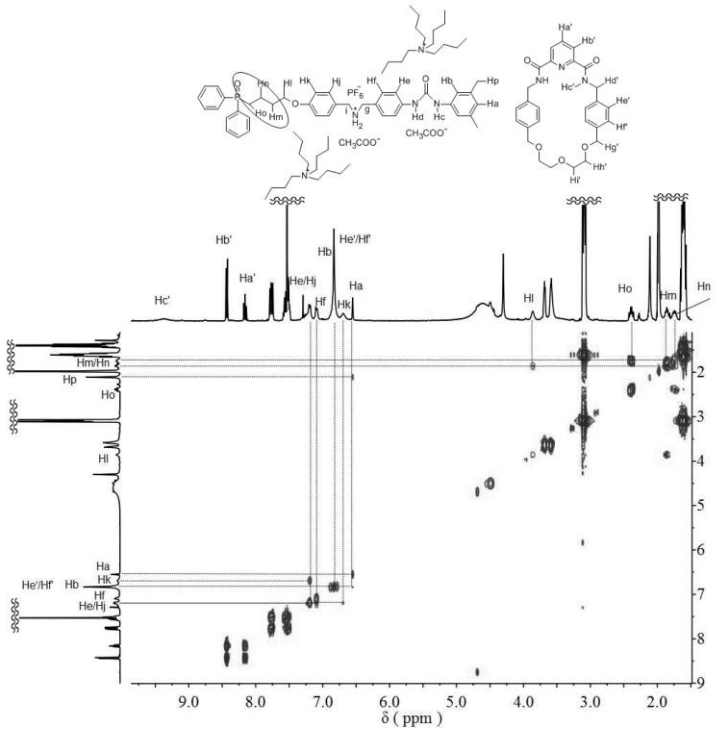


Fig. S31 Partial 2D COSY spectrum ($CDCl_3/CD_3CN$ = 1:1, 400 MHz, 298 K) of [**1**-H][PF_6] after the addition of 3.0 equiv. of TBAA.

8. X-Ray Data for [1-H][PF6]

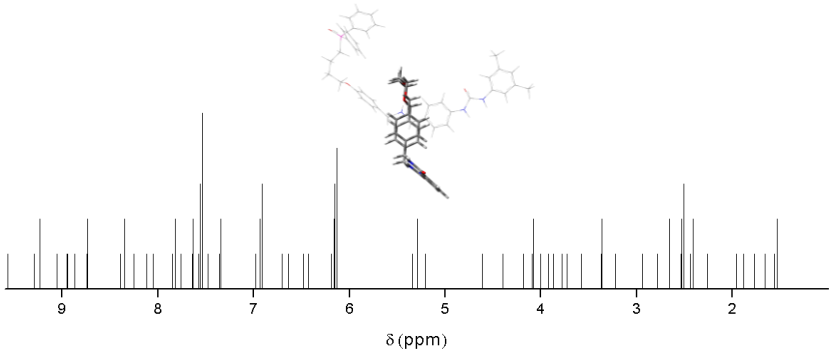
Table 1. Crystal data and structure refinement for [**1**-H][PF_6]

CCDC number	900778
Empirical formula	$C_{66}H_{74}N_6O_{10}F_6P_2$
Formula weight	1289.27
Temperature	296(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
a	14.9639(11)
b	16.2074(10)
c	16.6904(12)
α	68.0740(10)
β	65.602(2)
γ	86.2270(10)
Volume	3400.9(4) $Å^3$
Z	2
Density (calculated)	1.259
Absorption coefficient	0.140
F(000)	1356.0
Crystal size	0.28 × 0.24 × 0.22 mm^3
Theta range for data collection	2.34 to 22.15 °
Index ranges	-16<=h<=18, -18<=k<=19, -0<=l<=20
Reflections collected	37275
Independent reflections	13369 [R(int) = 0.0425]
Completeness to theta = 26.00 °	100.0 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on *F*2
Goodness-of-fit on *F*2	1.117
Final R indices [*I* > 2sigma(*I*)]	*R*1 = 0.0577, *wR*2 = 0.1132
R indices (all data)	*R*1 = 0.0837, *wR*2 = 0.1186
Largest diff. peak and hole	0.185 and -0.599 e ·$Å^{-3}$

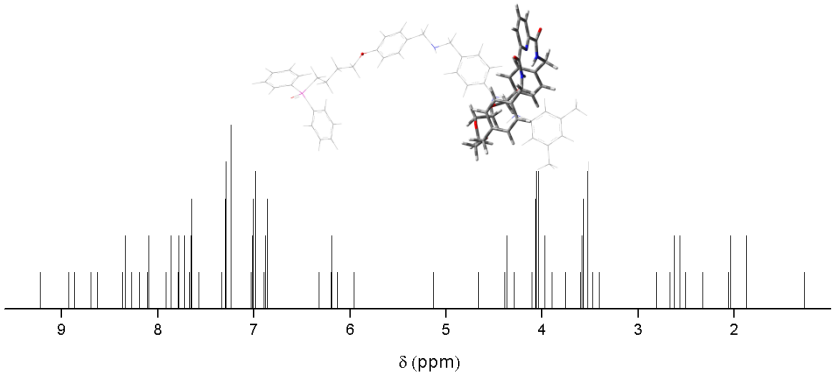
9. Theoretical calculations

All calculations were performed with the Gaussian 09 program suite[S6].

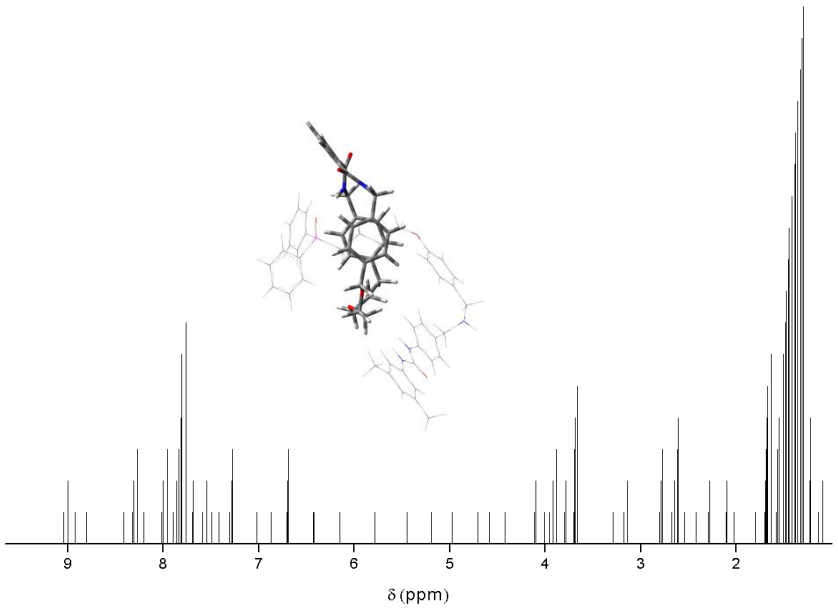
a)



b)



c)



d)

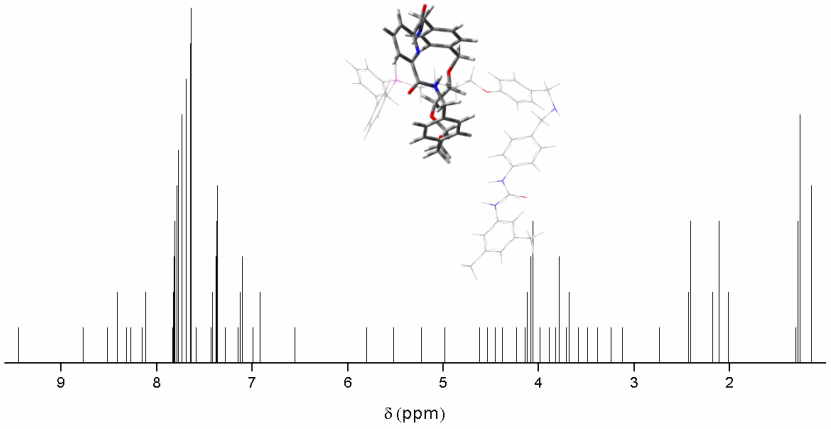
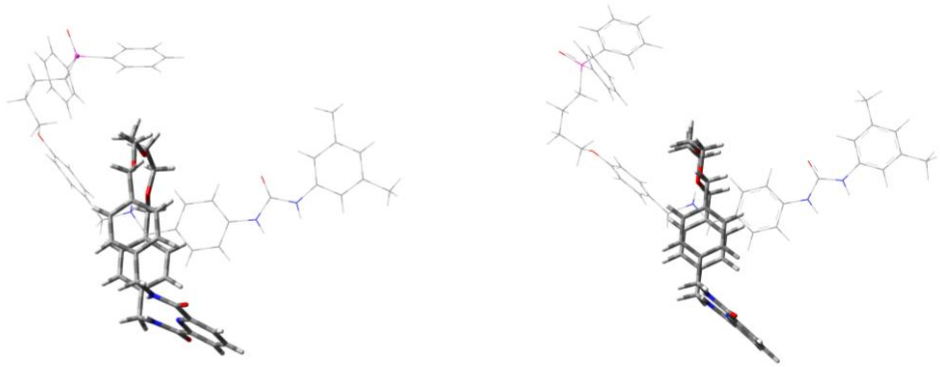


Fig. S32 The optimized structures and DFT-calculated chemical shifts of ^{1}H of three different stations a) State **I**, b) State **II**, c) State **III**, and d) State **III'**.



Crystal structure of state **I** Optimized structure of state **I**

Fig. S33 The crystal structure (left) and the geometry optimized structure by theoretical calculations (right) for molecular shuttle at State **I**.

10. References

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