Electronic Supplementary Information

Highly Efficient Synthesis of A Tristable Molecular Shuttle and Its Controlled Motion by Chemical Stimuli

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1. General Information

Commerically available solvents and chemicals were used without further purification unless stated. Where dry solvents were used, they were degassed with Ar, dried by 4 Å molecular sieves activated under 500 °C for 6 hours. Melting points were not corrected. All yields were given as isolated yields. Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet).

2. Complexation of S1 and M under the Presence of K^+

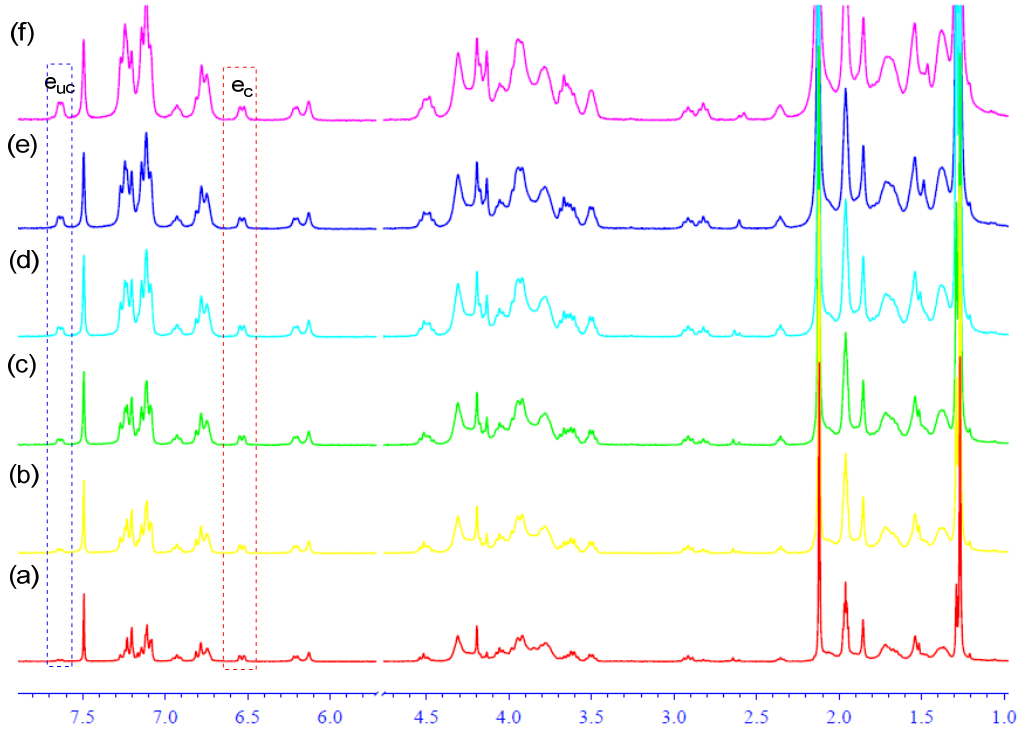


Fig. S1 Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of mixture of **S1** and **M** in the presence of K^+ at mole ratio of [**S1**]/[**M**] = : (a) 1.2; (b) 1.4; (c) 1.6; (d) 1.8; (e) 2.0; (f) 2.2. ($[\mathbf{M}]_0$ = 3.0 mM, and $[KPF_6]$ = 20.0 mM. The binding constant was calculated on the basis of the assumption that the binding of K^+ to **M** is essentially complete in a solution of **M** containing a large excess of potassium salts.)

3. ^{1}H NMR, ^{13}C NMR, HSQC, HMBC, and ROESY Spectra Analysis of Three Stable States of the [2]rotaxane

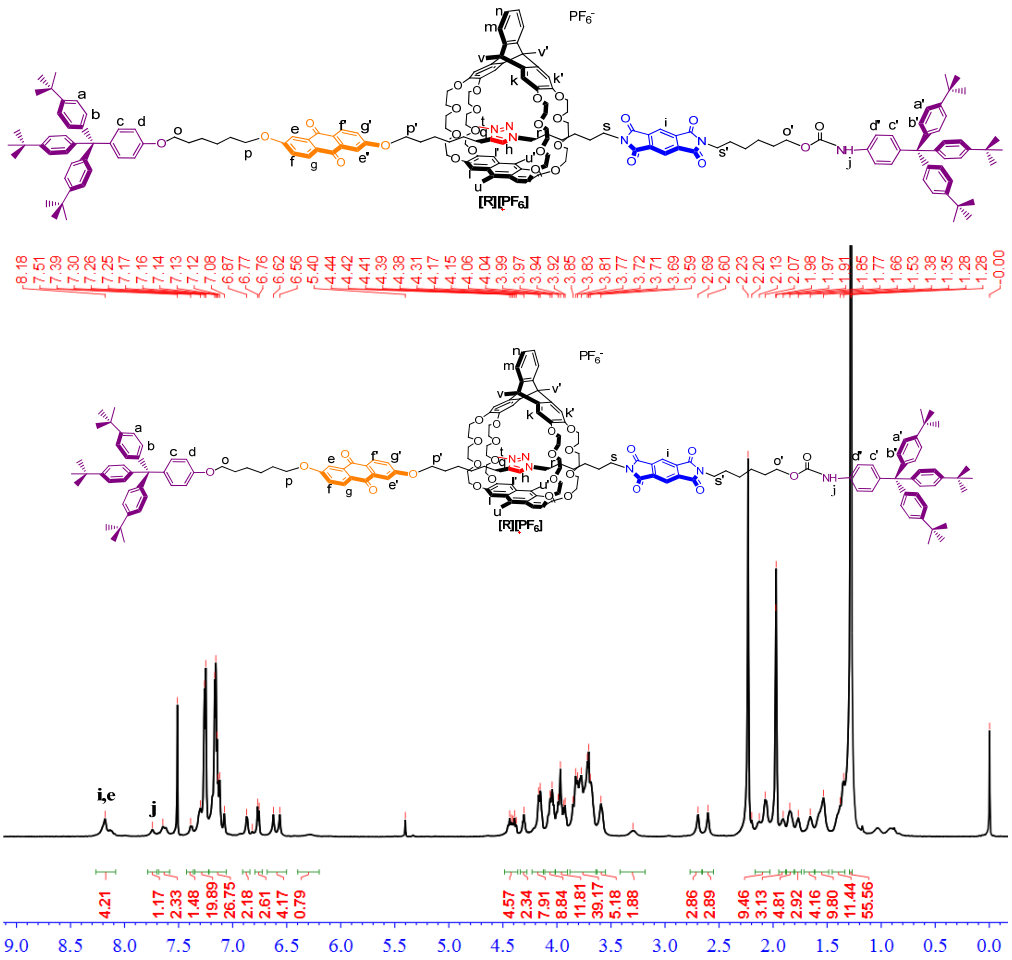


Fig. S2 ^{1}H NMR spectrum ($CDCl_3$/CD_3CN=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6].

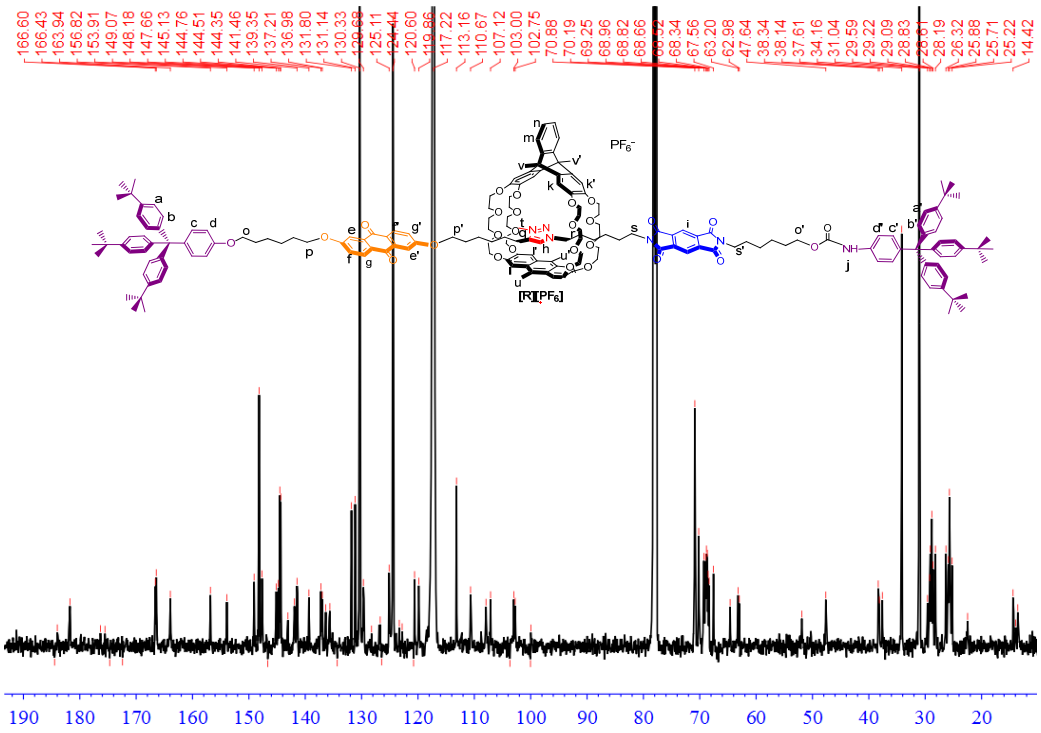
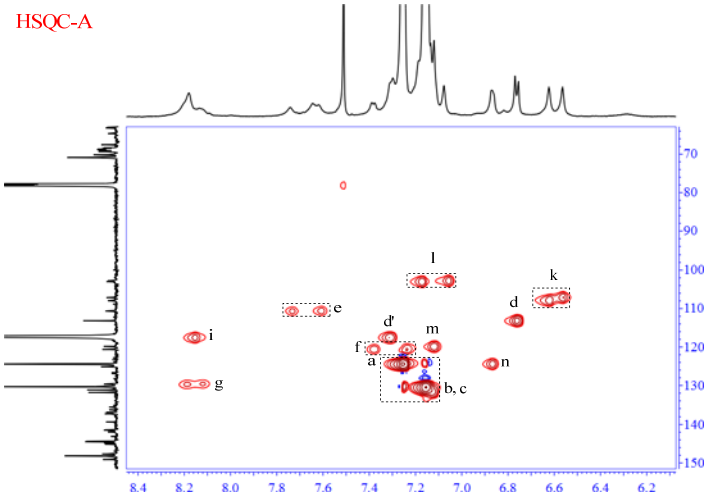


Fig. S3 ^{13}C NMR spectrum ($CDCl_3/CD_3CN$=1:1, 150 MHz, 278 K) of [2]rotaxane [**R**][PF_6].



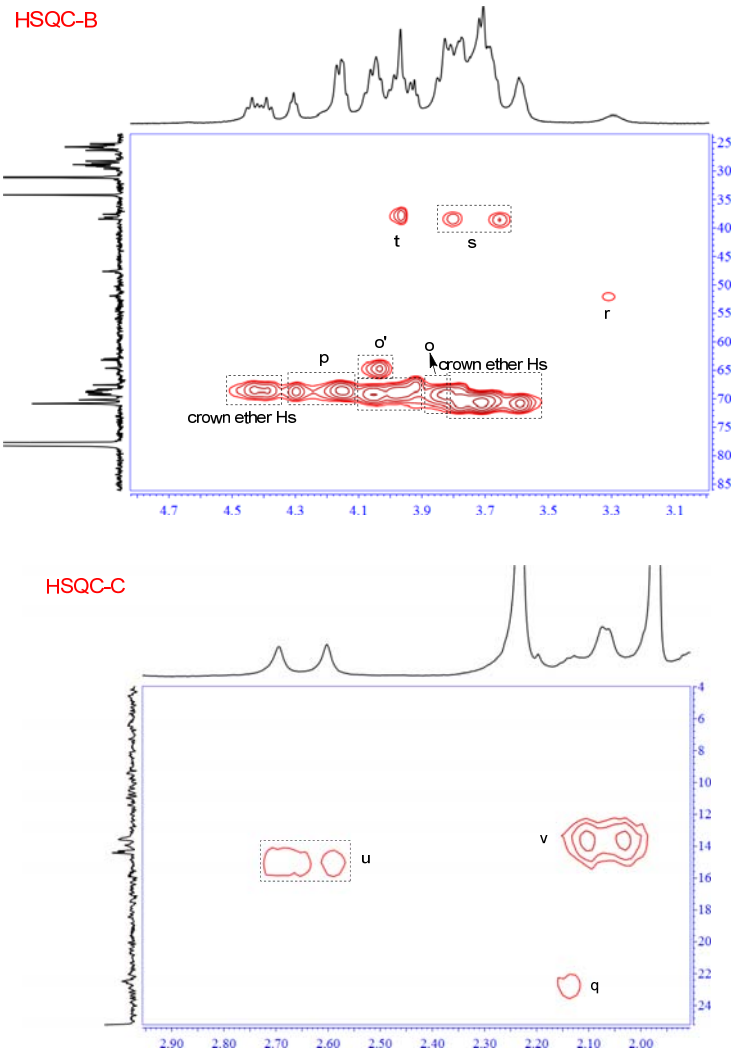


Fig. S4 HSQC spectrum ($CDCl_3$/CD_3CN=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6].

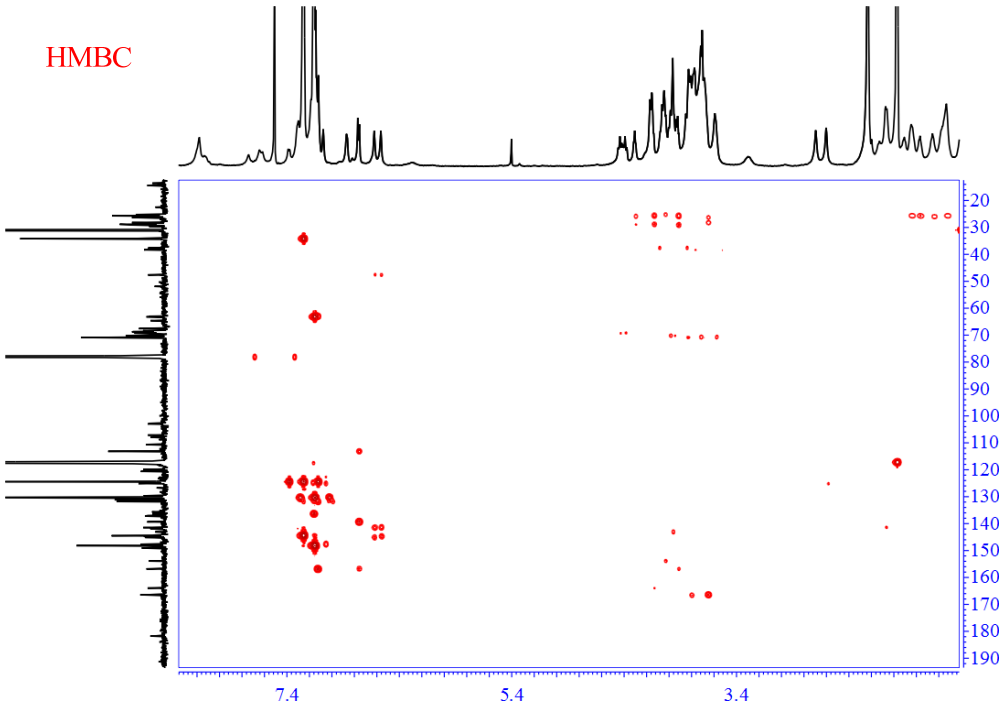
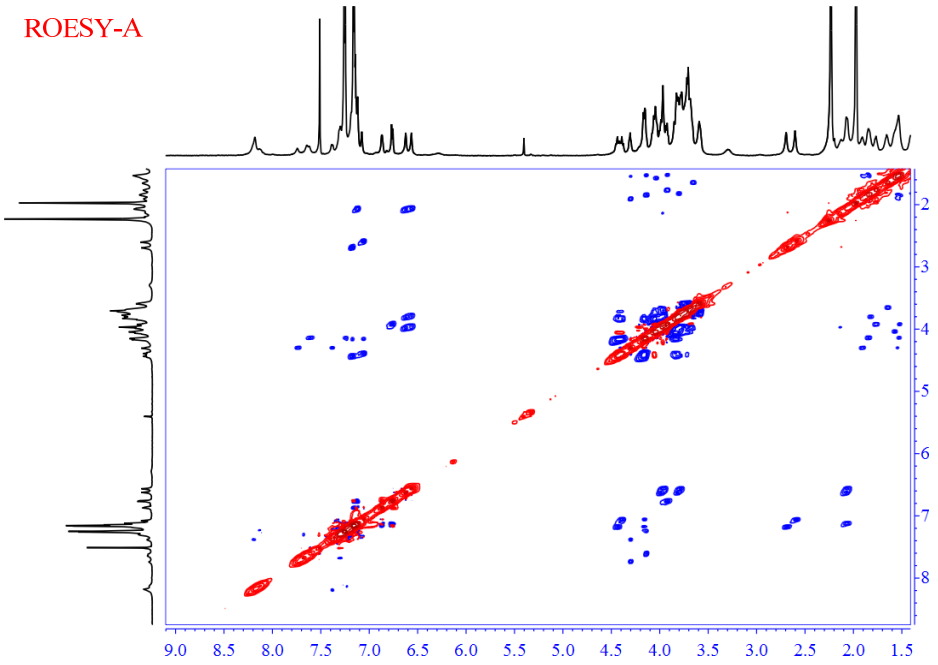


Fig. S5 HMBC spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6].



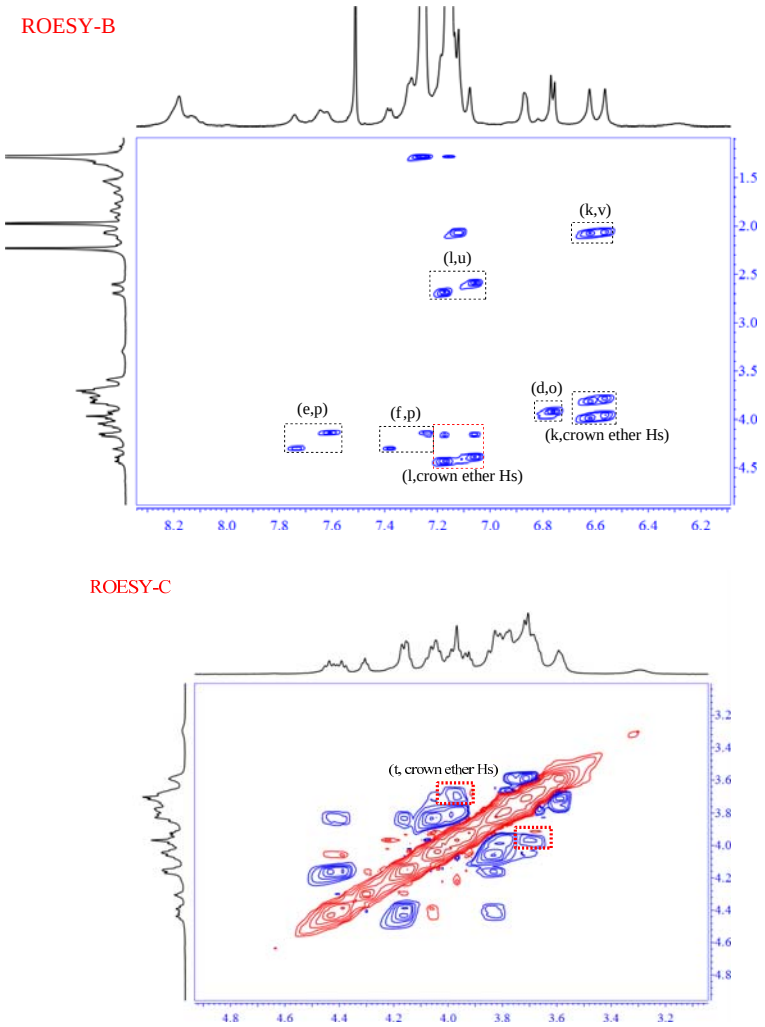


Fig. S6 ROESY spectra ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6].

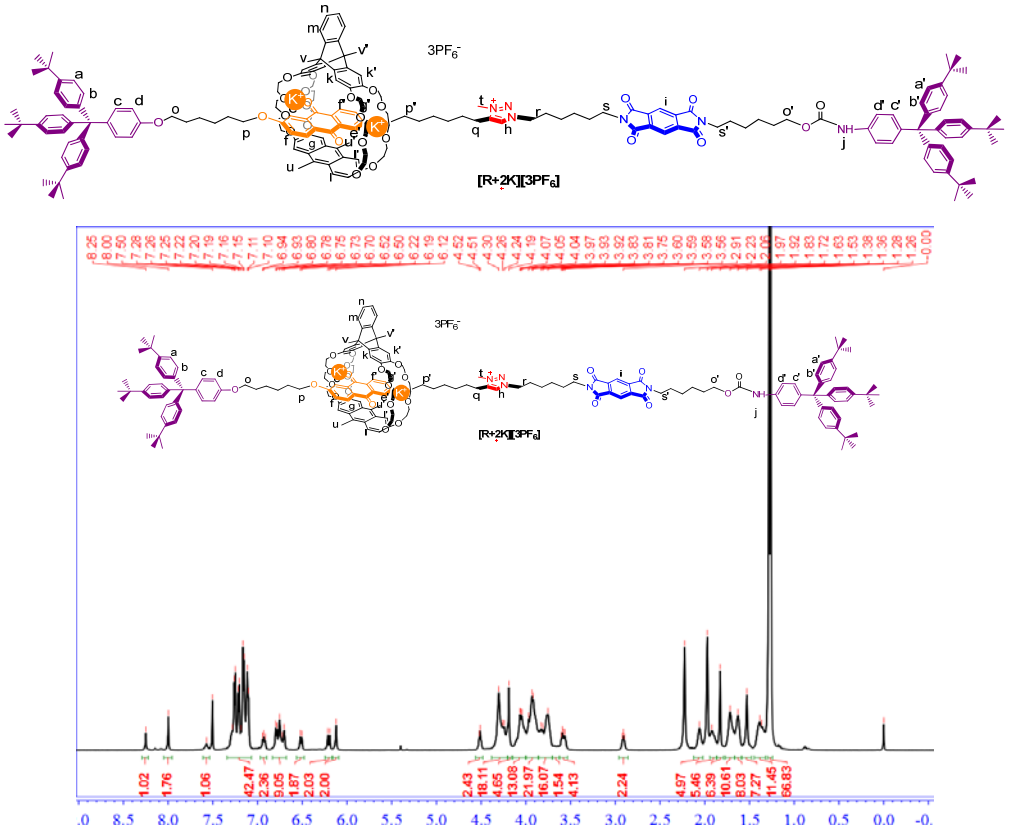


Fig. S7 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of KPF_6.

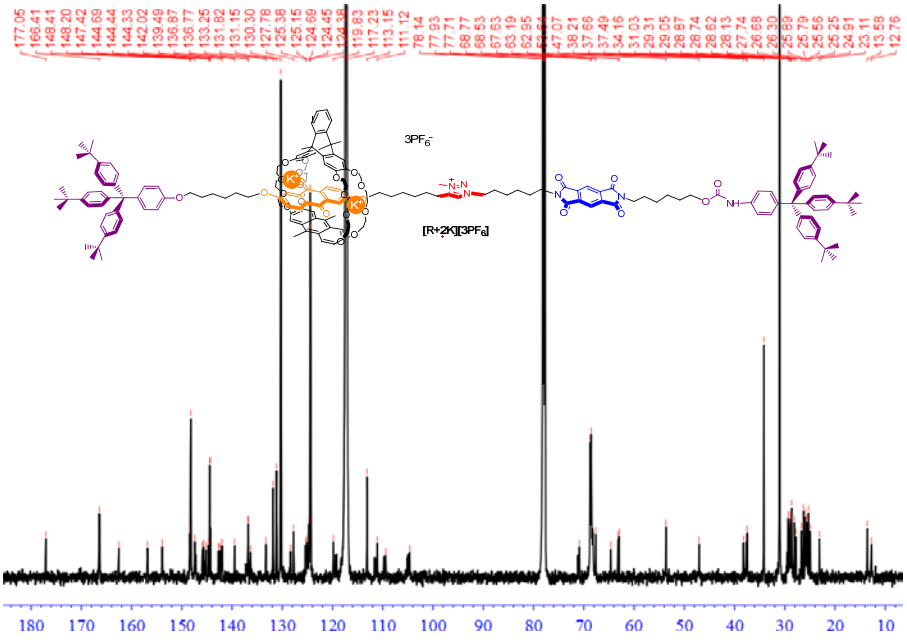


Fig. S8 ^{13}H NMR spectrum ($CDCl_3/CD_3CN$=1:1, 150 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after

the addition of 4.0 equivalents of KPF_6.

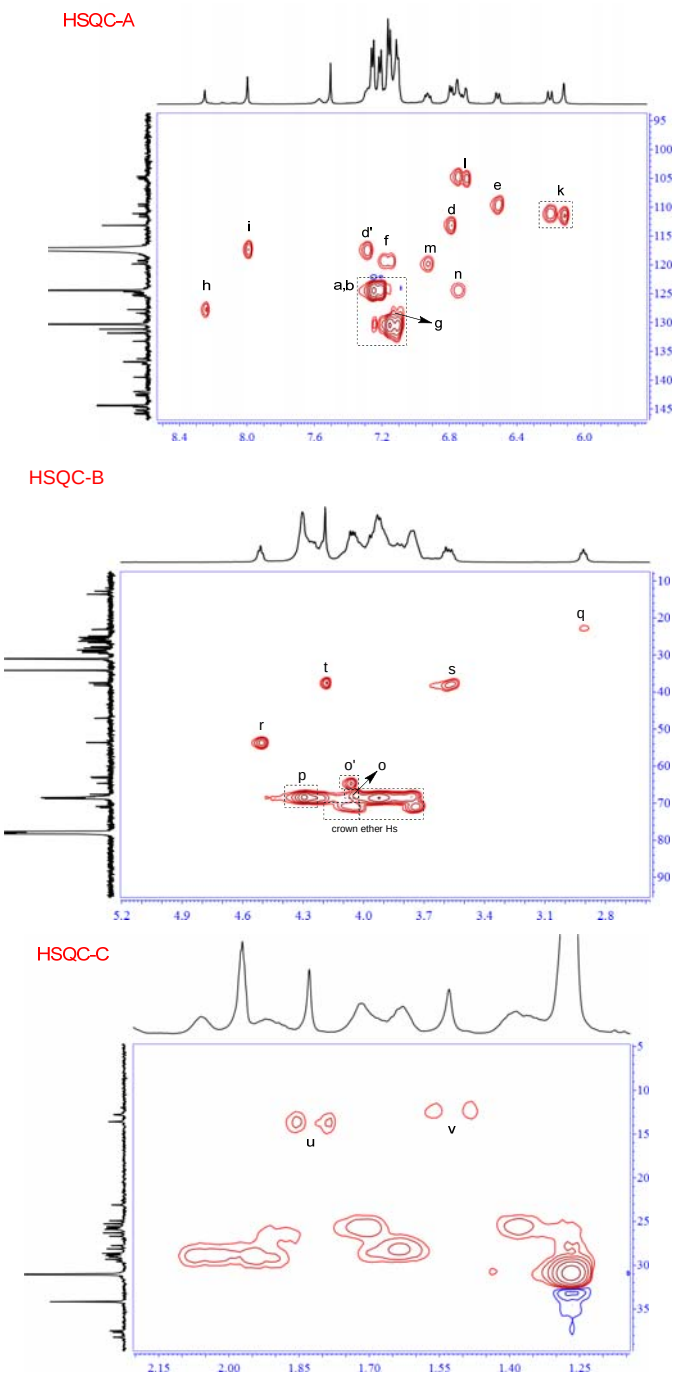


Fig. S9 HSQC spectra ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0equivalents of KPF_6.

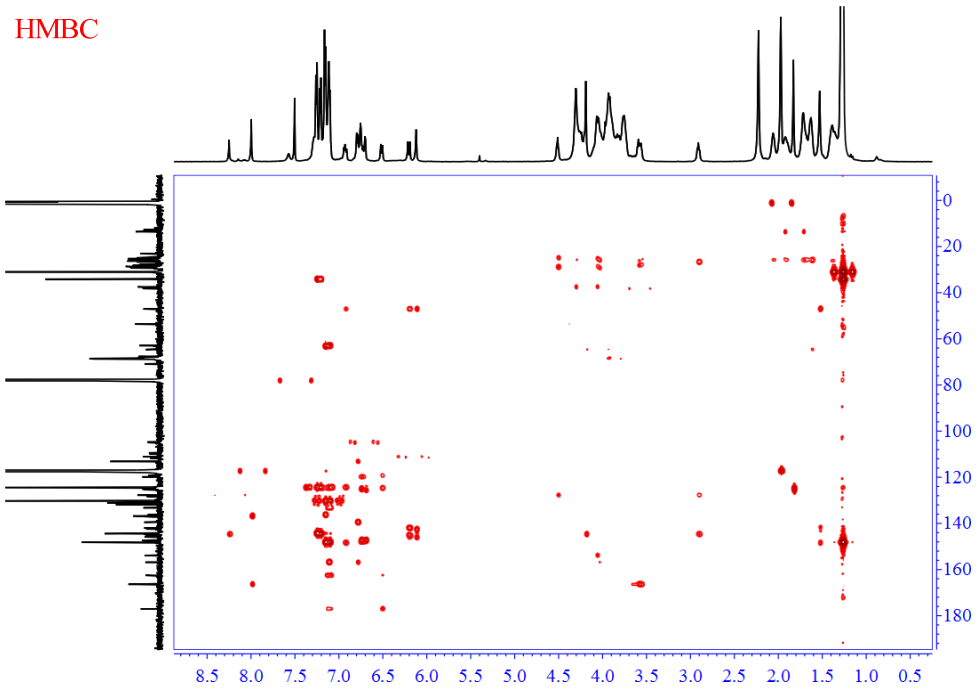


Fig. S10 HMBC spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0equivalents of KPF_6.

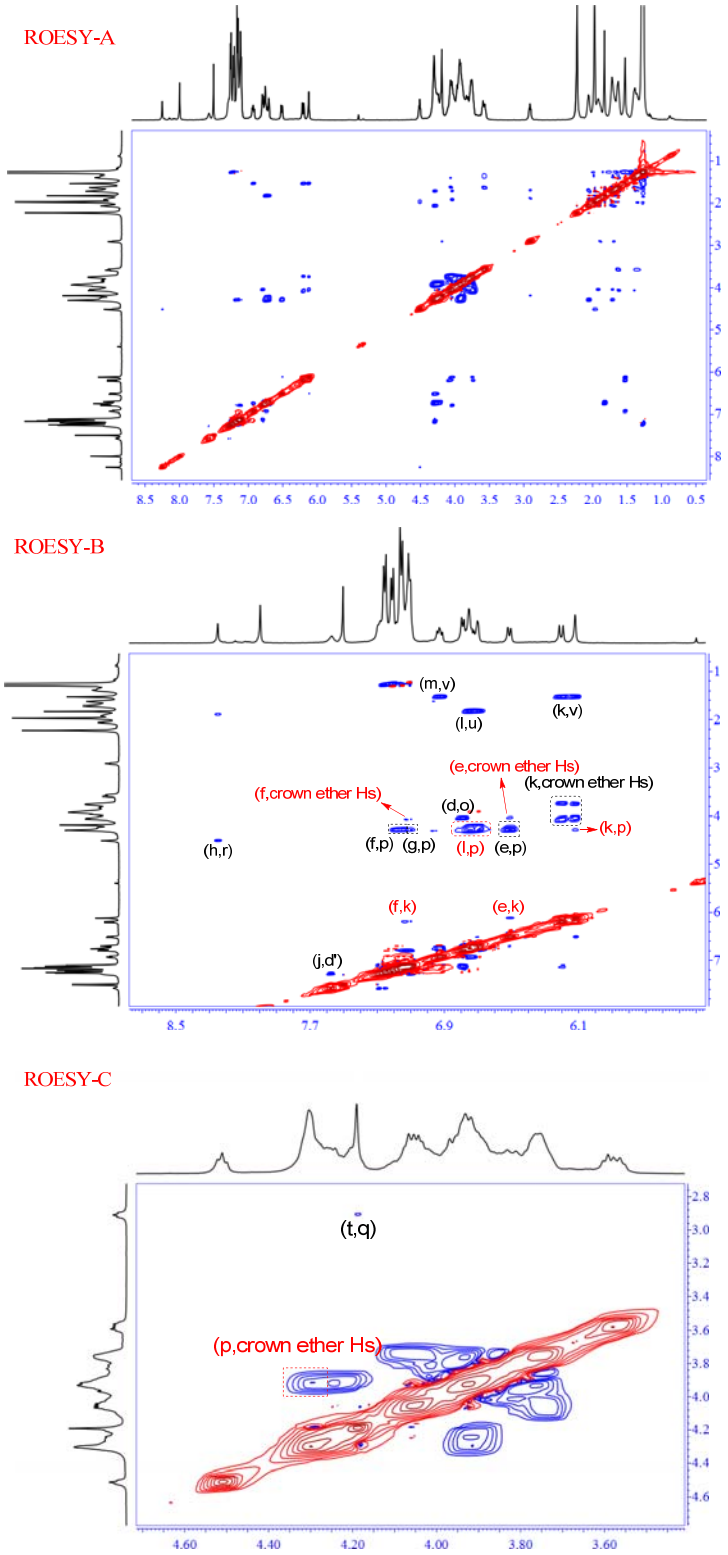


Fig. S11 ROESY spectra ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of KPF_6.

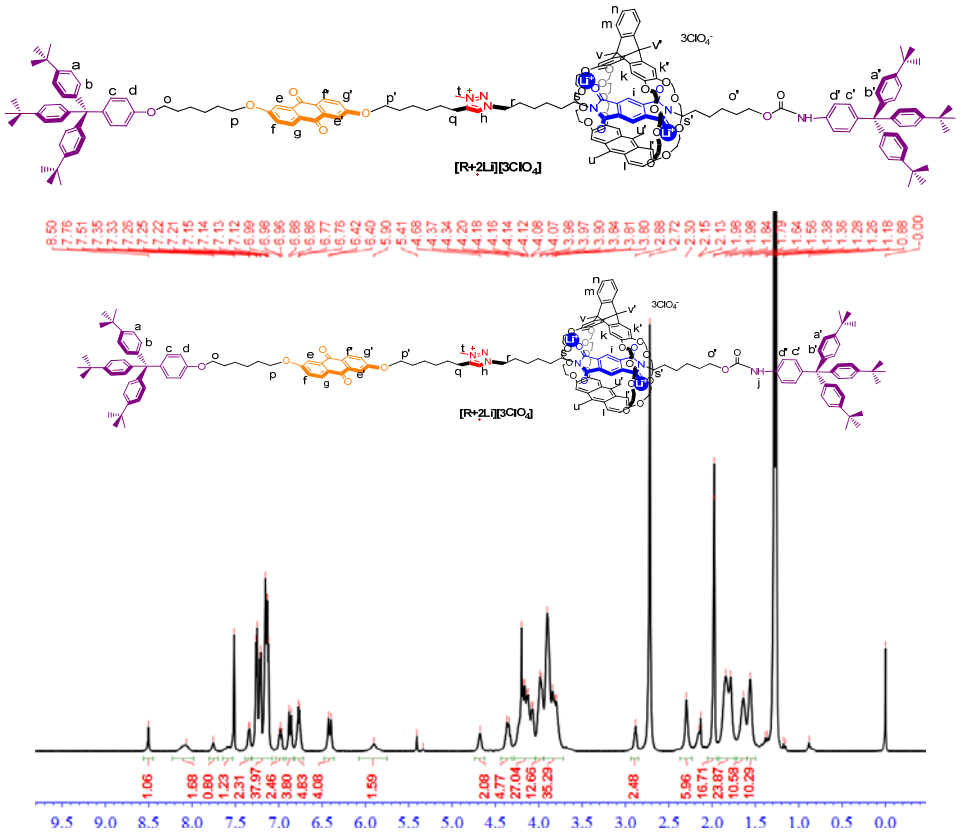


Fig. S12 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of $LiClO_4$.

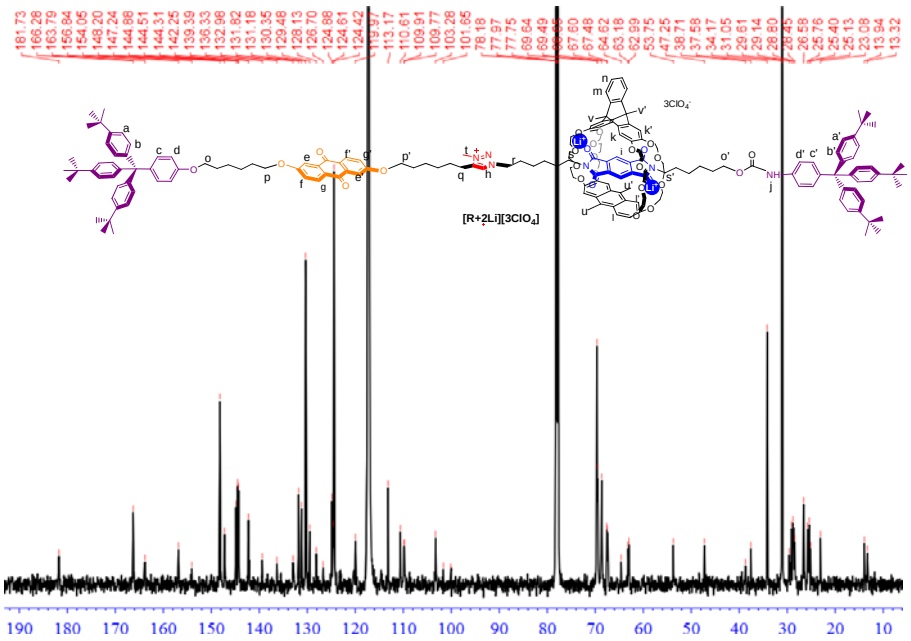


Fig. S13 ^{13}C NMR spectrum ($CDCl_3/CD_3CN$=1:1, 150 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of $LiClO_4$.

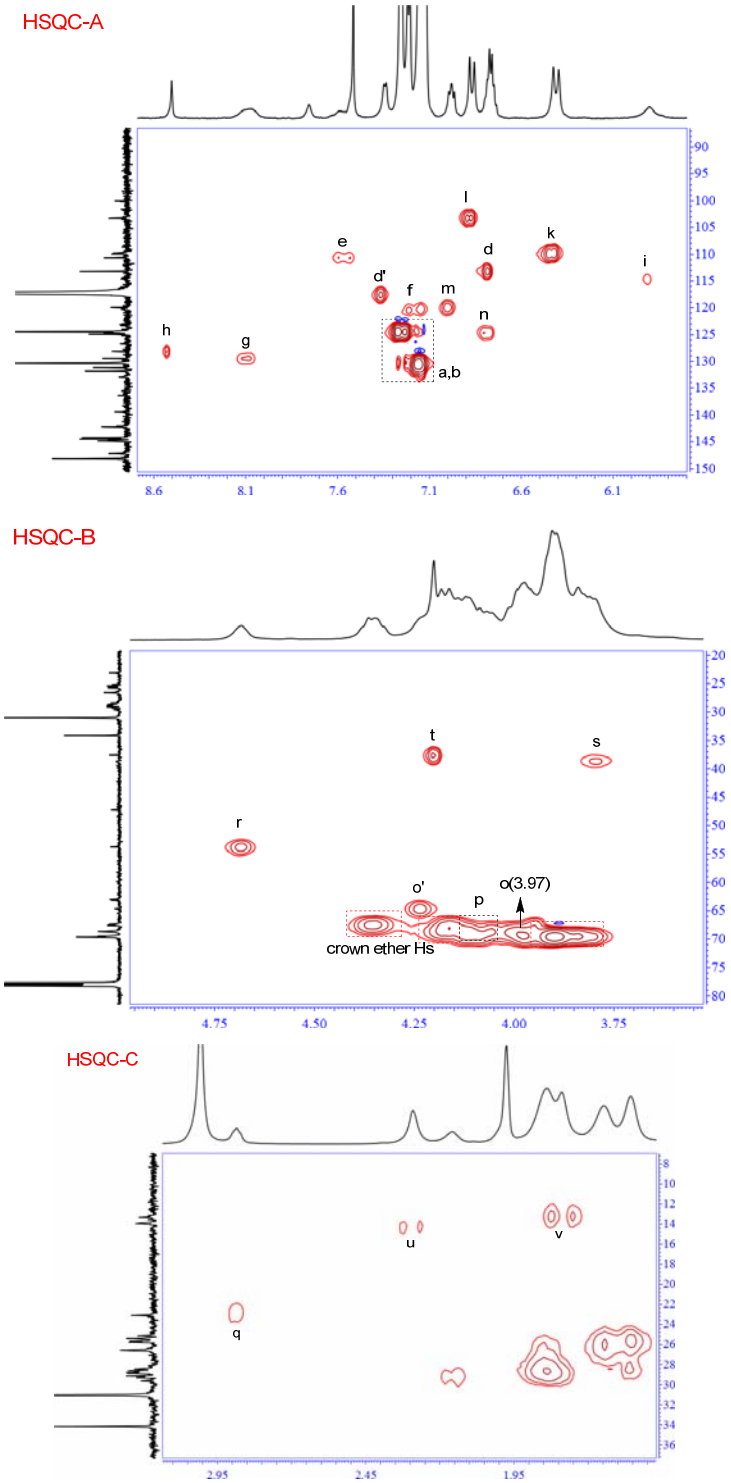


Fig. S14 HSQC spectra ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of $LiClO_4$.

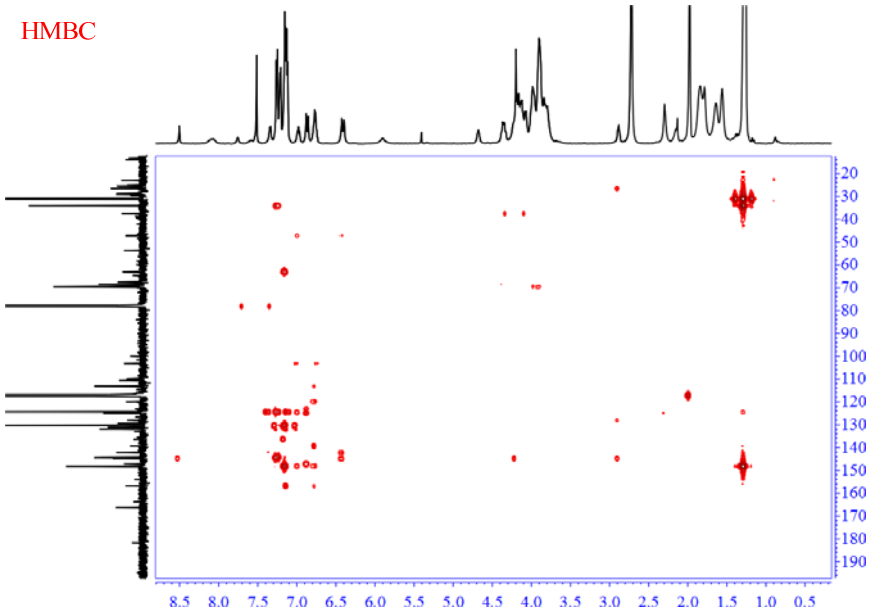
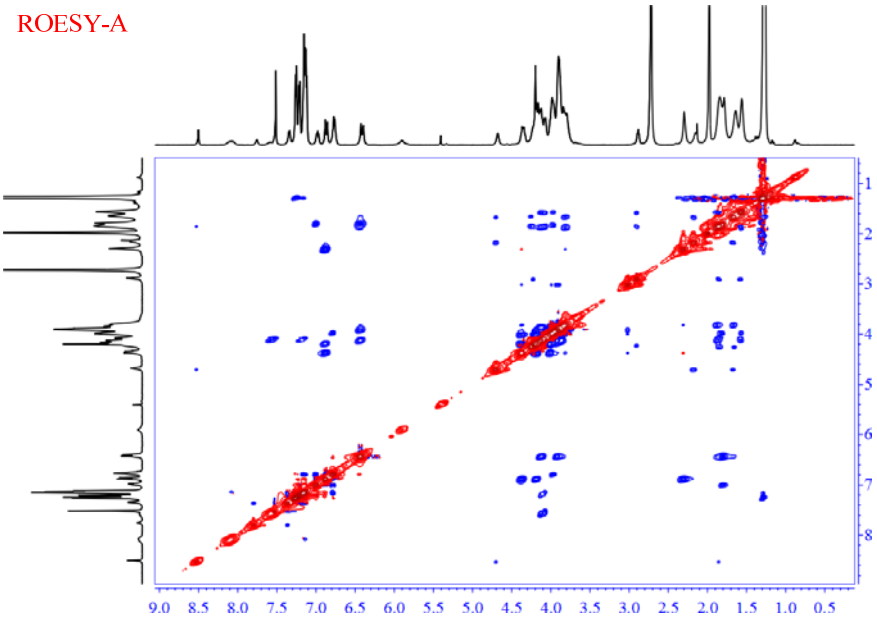


Fig. S15 HMBC spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of $LiClO_4$.



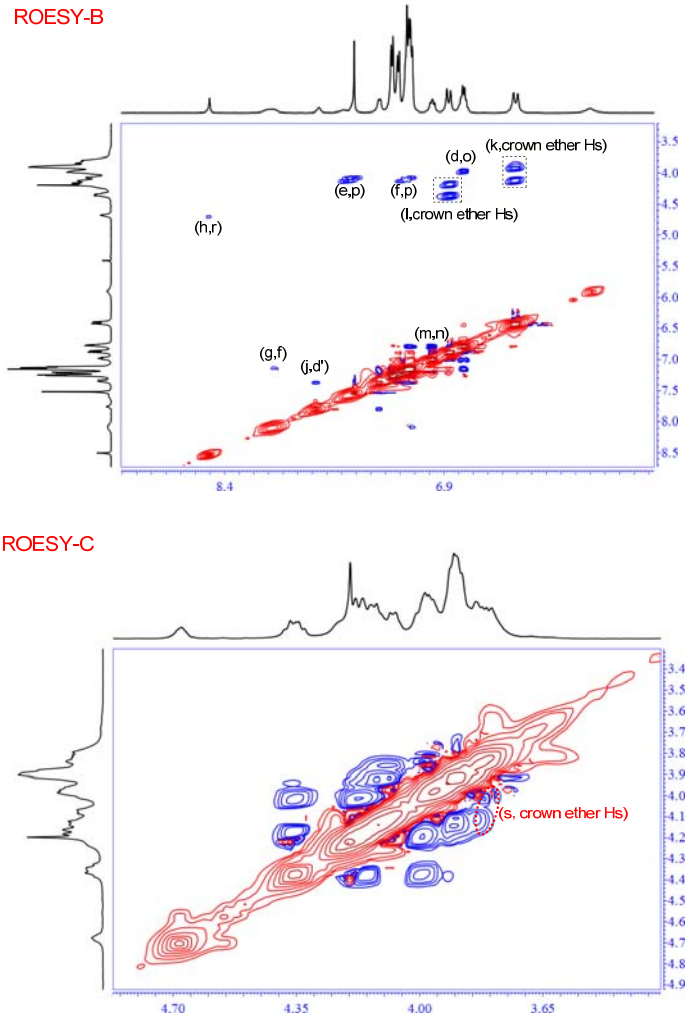


Fig. S16 ROESY spectra ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of [2]rotaxane [**R**][PF_6] after the addition of 4.0 equivalents of $LiClO_4$.

4. HRMS Spectra for Three States of the [2]rotaxane

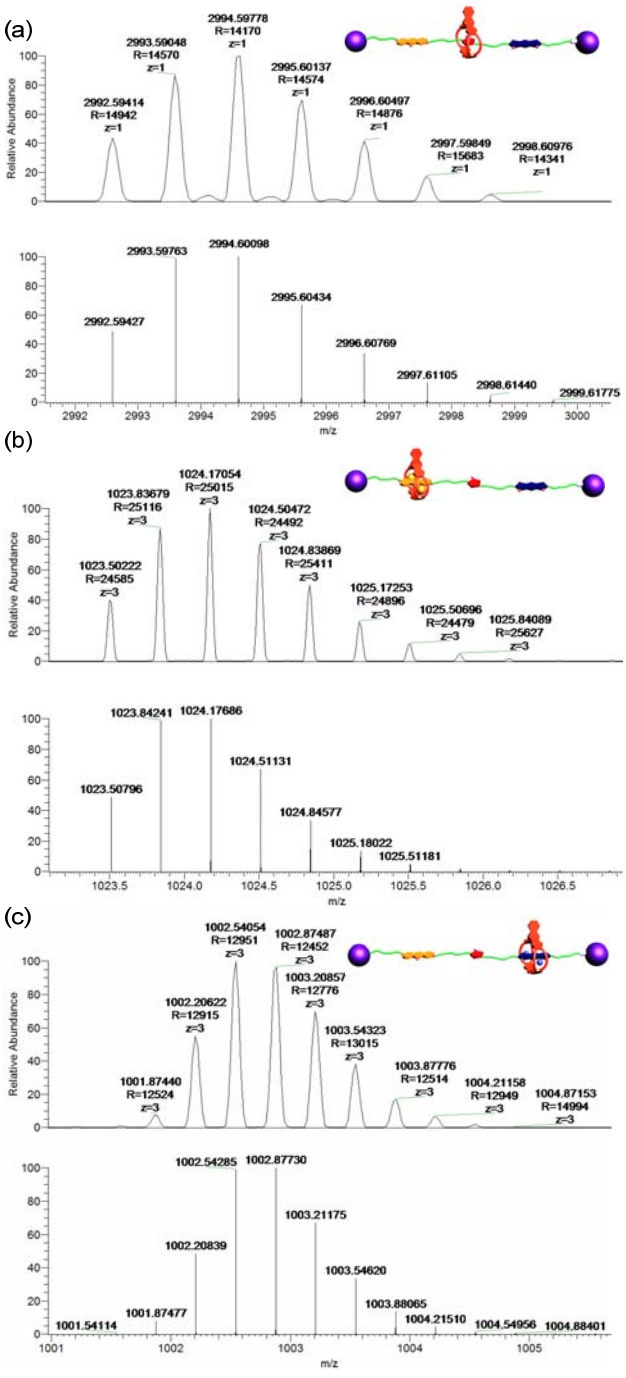


Fig. S17 High-resolution electrospray ionization (HR-ESI) mass spectrometry: isotopic distribution with peaks at m/z (a) 2994.5978, (b) 1024.1705 and (c) 1002.8749 corresponding to the positively charged ion peaks $[\mathbf{R}]^{+}$, $[\mathbf{R}+2K]^{3+}$ and $[\mathbf{R}+2Li]^{3+}$, respectively. Experimental (top) and calculated (bottom).

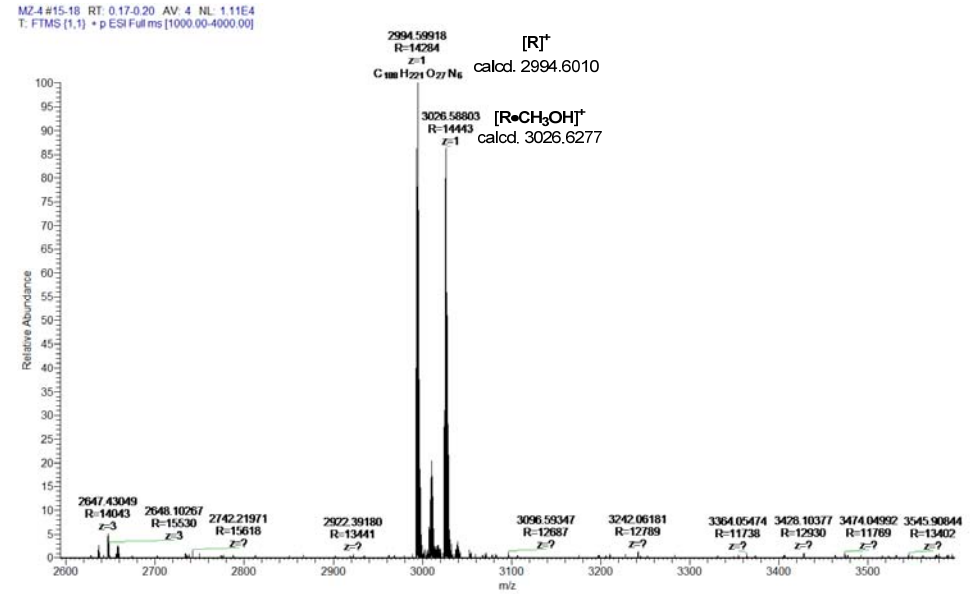


Fig. S18 HRMS spectrum of [2]rotaxane [**R**][PF_6]

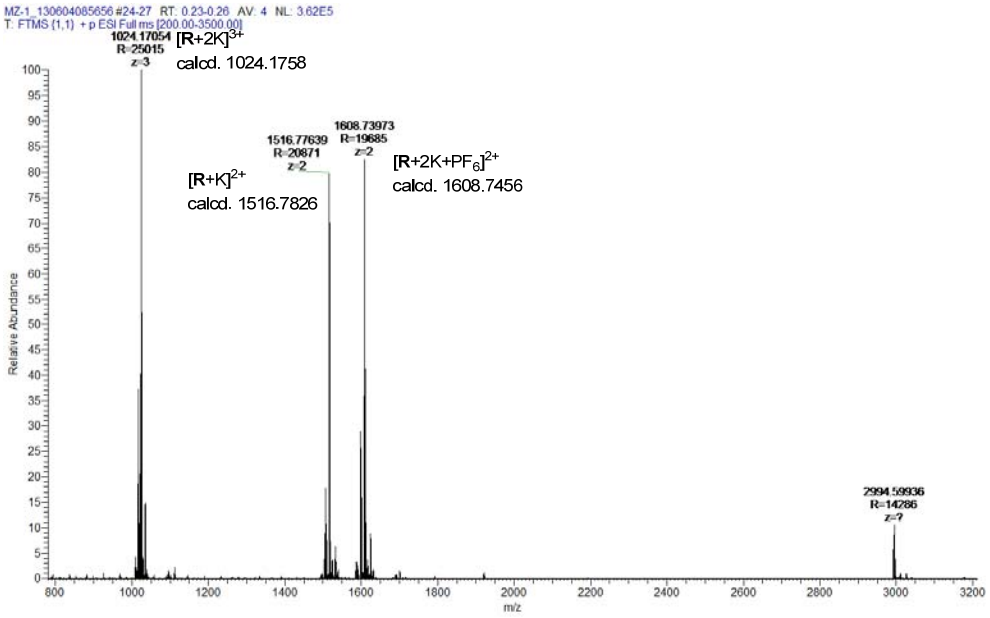


Fig. S19 HRMS spectrum of [2]rotaxane [**R**][PF_6] in the presence of 4.0 equivalents of KPF_6.

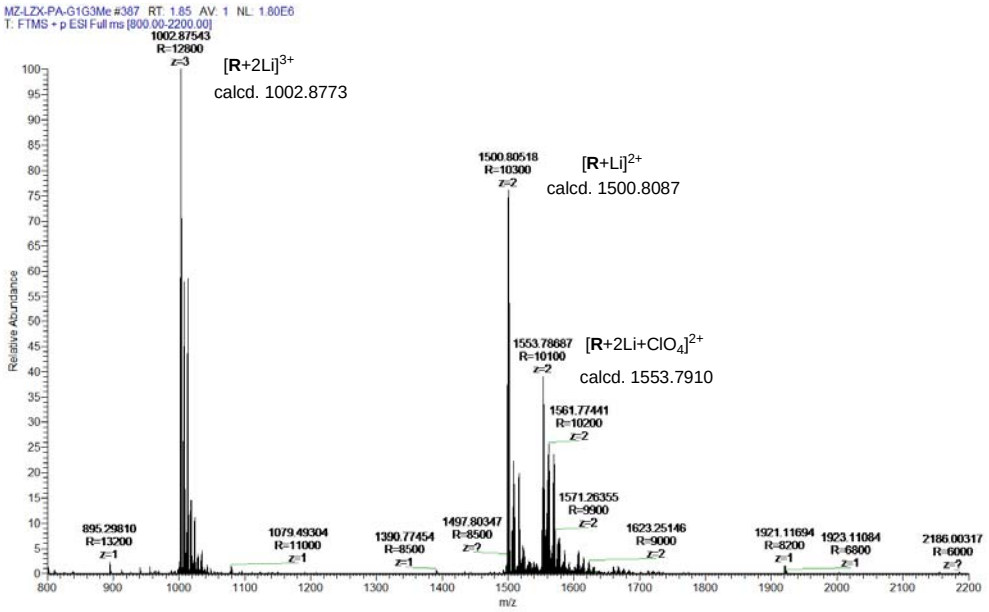


Fig. S20 HRMS spectrum of [2]rotaxane [**R**][PF_6] in the presence of 4.0 equivalents of $LiClO_4$.

5. NMR Spectra for Other New Compounds

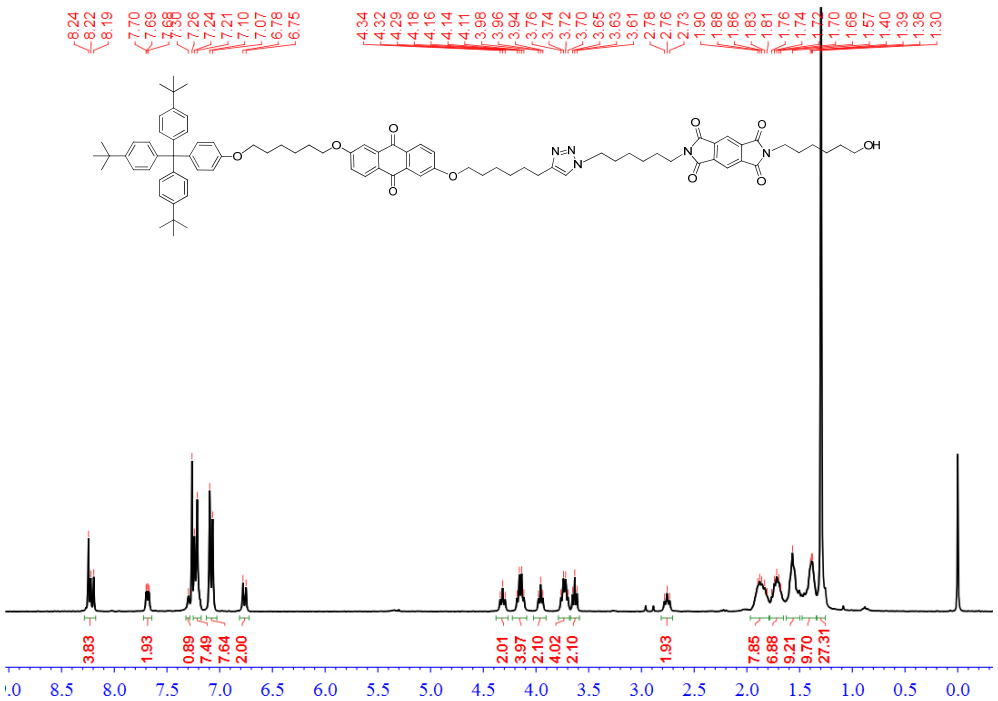


Fig. S21 ^1H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of **3**.

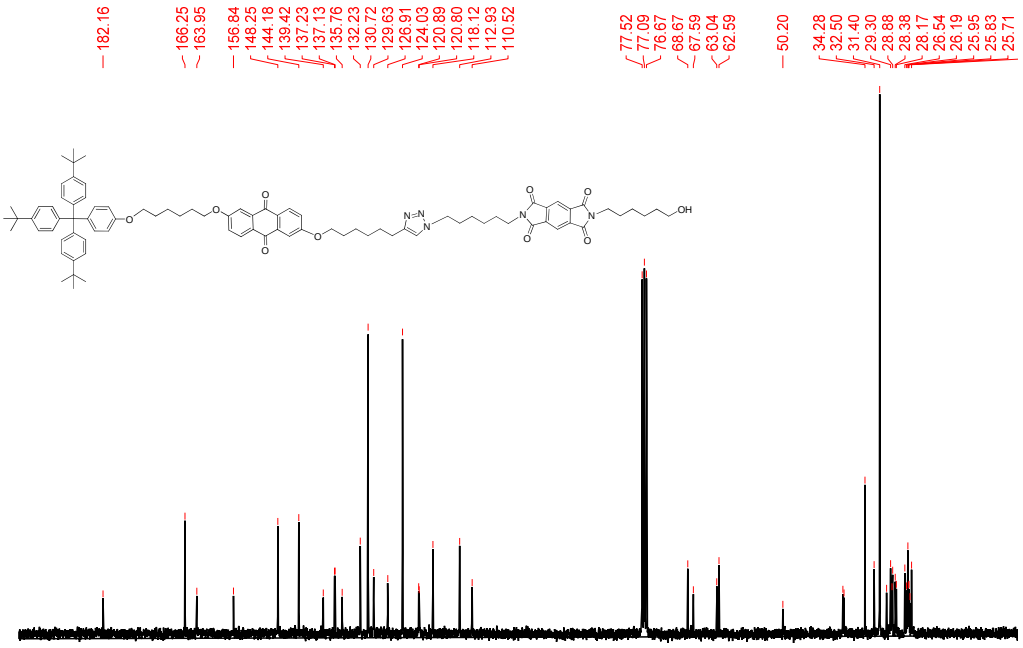


Fig. S22 ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of **3**.

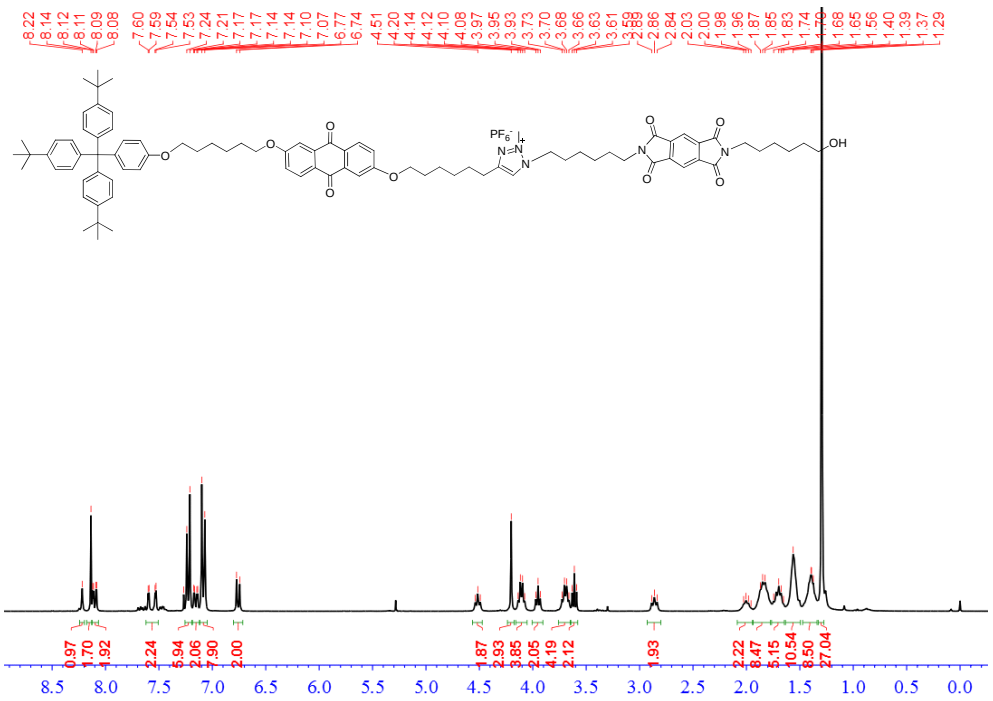


Fig. S23 ^{13}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of **S1**.

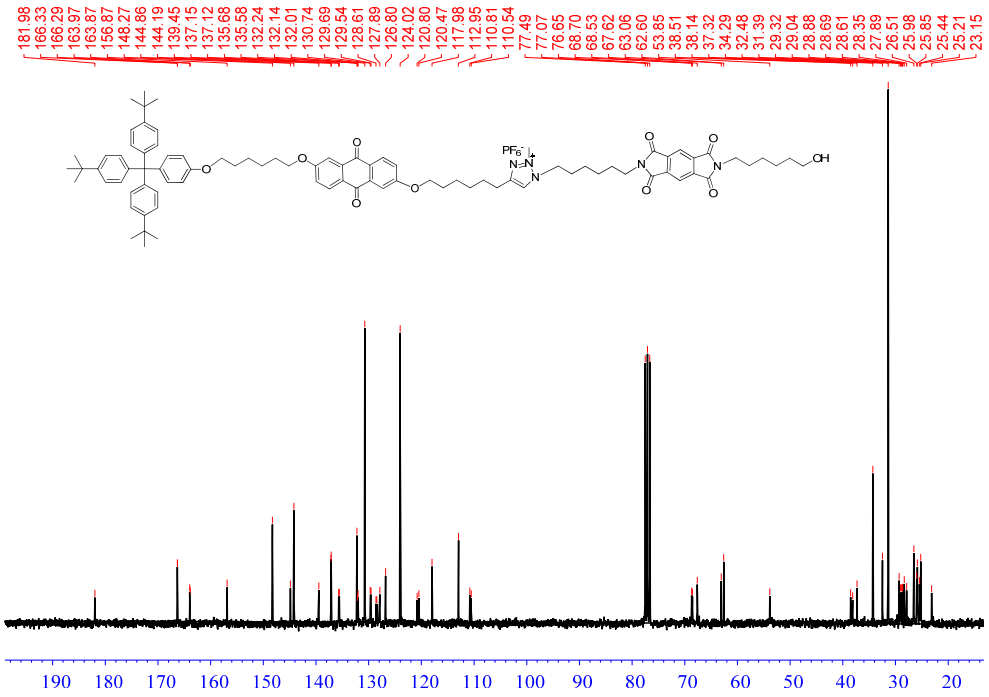


Fig. S24 ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of **S1**.

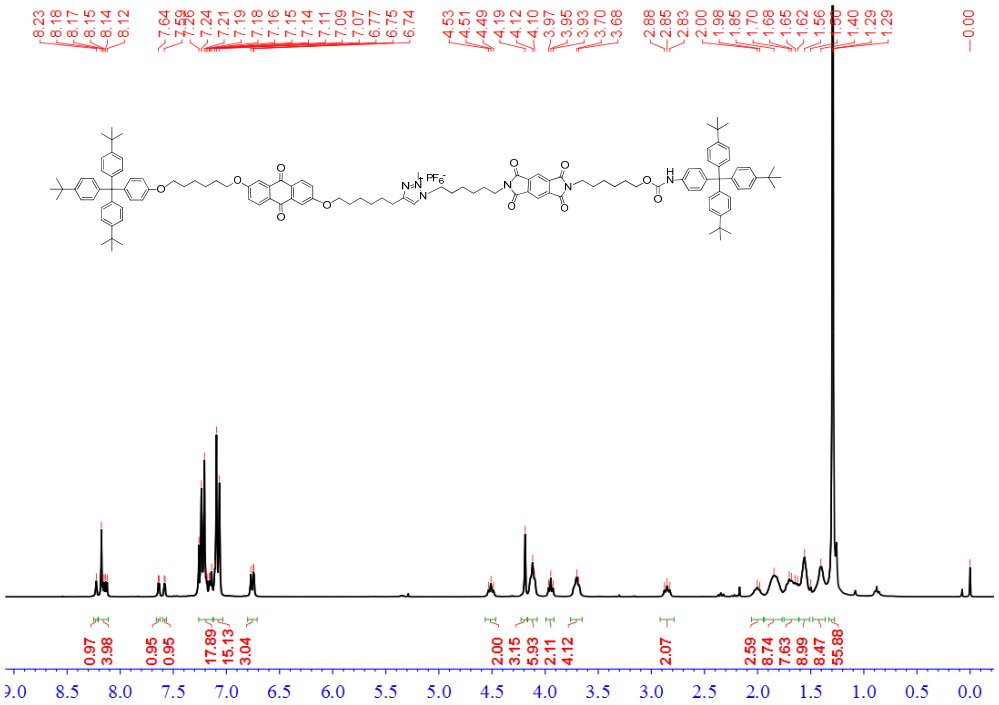


Fig. S25 ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of **S**.

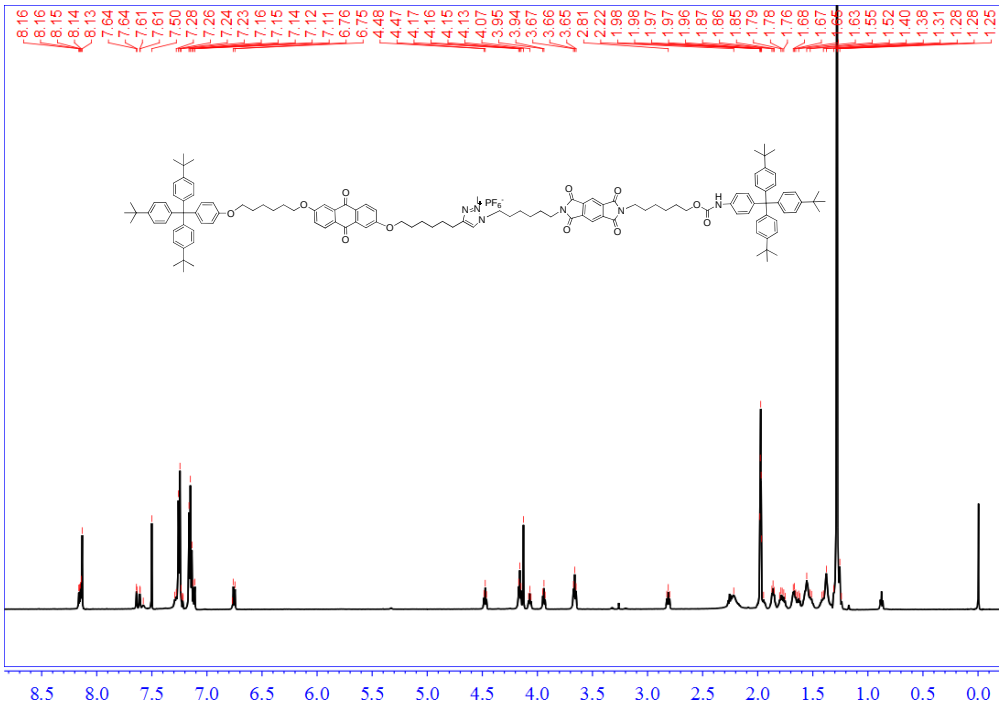


Fig. S26 ^{1}H NMR spectrum ($CDCl_3/CD_3CN$=1:1, 600 MHz, 278 K) of **S**.

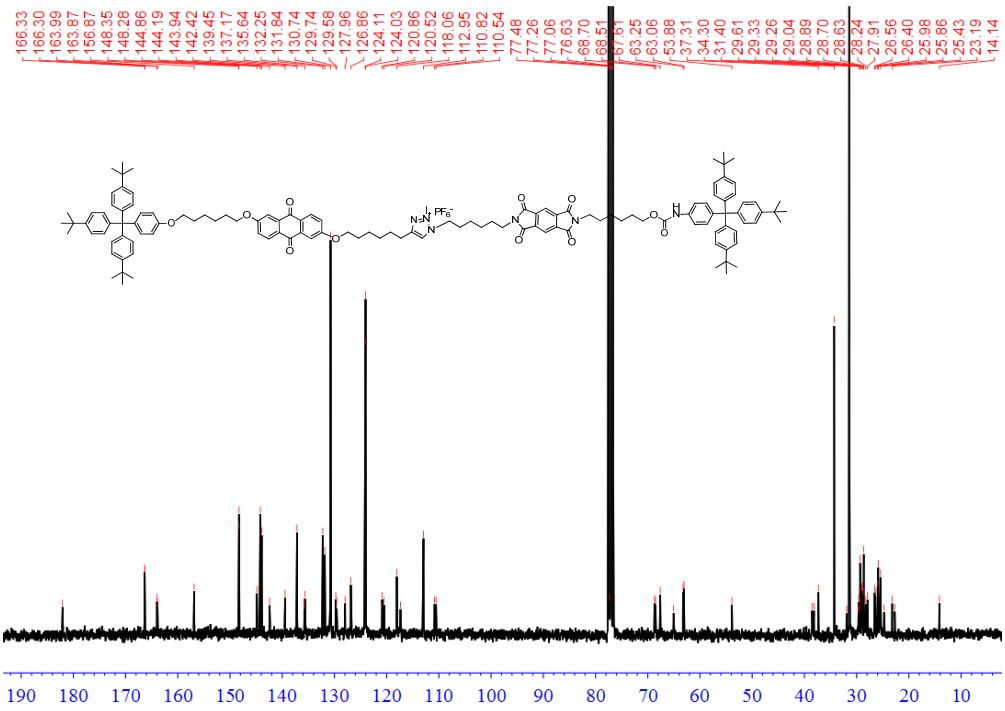


Fig. S27 ^{13}C NMR spectrum ($CDCl_3$, 75 MHz, 298 K) of **S**.