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Supplementary Information
Fig. S1. ESI-mass spectrum of R-H·PF₆ showing a [M–PF₆]⁺ molecular ion peak.

Fig. S2. UV/visible spectra (conc. = 0.02 mM in MeCN).
**Fig. S3.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components in the presence of excess H$_2$O (conc. = 0.02 mM in MeCN).

**Fig. S4.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).
**Fig. S5.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).

**Fig. S6.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).
Fig. S7. A plot of the reciprocal of rotaxane R-H·PF₆ concentration (M⁻¹) in CD₃CN versus time (h). The activations within first one hour can be fitted into straight lines, leading to second order kinetics.

Fig. S8. Partial ¹H NMR spectrum (400 MHz, CD₃CN, 295 K) of R-H·PF₆ in the presence of excess of HCl/Et₂O (0.1 M) (f = free).
Fig. S9. Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 295 K) of $\textbf{R-H-PF}_6$ in the presence of 2 equiv. of toluidine ($f = \text{free}$).

Fig. S10. Stacked fluorescence emission of rotaxane $\textbf{R-H-PF}_6$ with different amounts of HPF$_6$/H$_2$O (0.1 M).
**Fig. S11.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).

**Fig. S12.** Fluorescence emission spectra (excitation wavelength = 290 nm) of Amine 1 (conc. = 0.02 mM in MeCN).
**Fig. S13.** Fluorescence emission spectra (excitation wavelength = 290 nm) of rotaxane R-H·PF₆ (conc. = 0.02 mM in MeCN).

**Fig. S14.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).
**Fig. S15.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).

**Fig. S16.** Fluorescence emission spectra (excitation wavelength = 290 nm) of components (conc. = 0.02 mM in MeCN).
$^1$H NMR (400 MHz, CDCl$_3$, 296 K) spectrum of 1
$^{13}$C NMR (101 MHz, CDCl$_3$, 296 K) spectrum of 1
$^1$H NMR (400 MHz, CD$_3$CN, 296 K) spectrum of 1-H·PF$_6$
$^{13}$C NMR (101 MHz, CD$_3$CN, 296 K) spectrum of 1-H·PF$_6$
$^1$H NMR (400 MHz, CDCl$_3$, 295 K) spectrum of 4
$^{13}$C NMR (101 MHz, CDCl$_3$, 295 K) spectrum of 4
$^1$H NMR (400 MHz, CDCl$_3$, 295 K) spectrum of 7
$^{13}$C NMR (101 MHz, CDCl$_3$, 296 K) spectrum of 7
$^1$H NMR (400 MHz, CD$_3$CN, 295 K) spectrum of rotaxane R-H·PF$_6$
$^{13}$C NMR (101 MHz, CD$_3$CN, 295 K) spectrum of rotaxane R-H·PF$_6$