Supporting Information

1. Experimental section

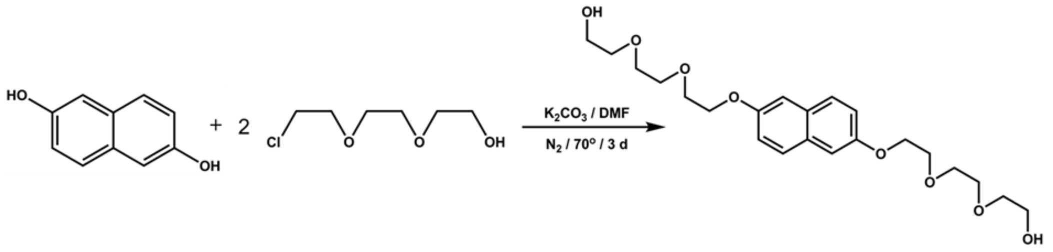
1.1 *chemicals*

2,6-Dihydroxynaphthalene, 2-(2-(2-chloroethoxy)ethoxy)ethoxyethanol and methylviologen were purchased from Sigma-Aldrich. 3-chloropropyltriethoxysilane was purchased from TCI. All other chemicals were obtained from Beijing Chemical Reagents Company and used without further purification. CB[8] was synthesized according to the procedure by Day and Kim. Deionized water was further purified with RF ultrapure water system. Quartz wafers (0.8 cm×3 cm) were used as substrates. Prior to use, these quartz wafers were put into a solution of H_2SO_4: H_2O_2=7:3 for 10min at 100°C. Then, these wafers were taken out of the solution, rinsed with plenty of deionized water and dried under a stream of N_2.

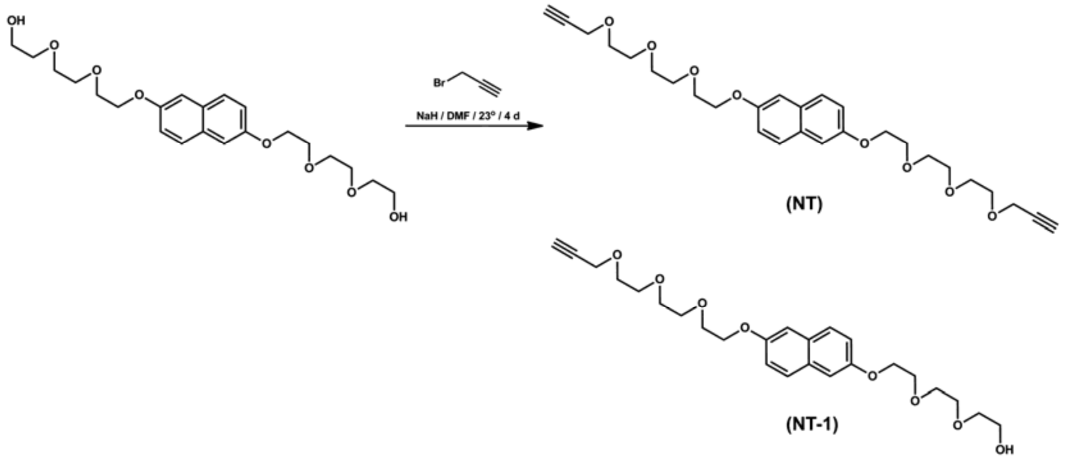
1.2 *Instrumentation*

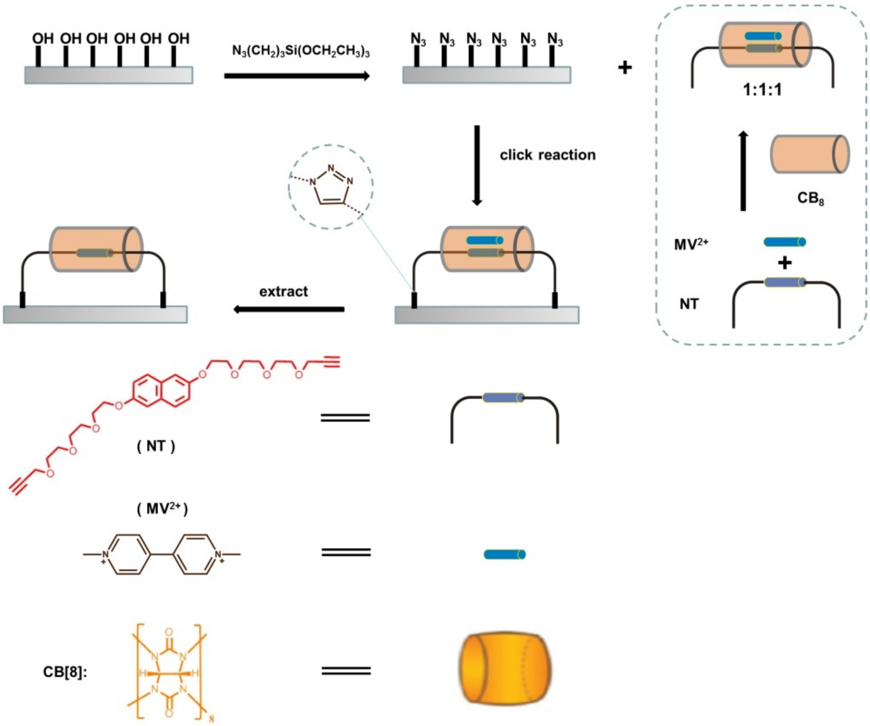
^{1}H NMR spectra were obtained using a JEOL JNM–ECA300 at 300 MHz, respectively. Electrospray ionization mass spectrometry (ESI-MS) was obtained by means of Bruker ESQUIRE-LC spectrometer. The UV–Vis absorption spectra were recorded using a Perkin-Elmer UV/VIS Lamda35 spectrometer. The fluorescence emission measurements were carried out using a fluorescence spectrometer (Perkin-Elmer LS55). The quartz wafer was placed in a quartz cuvette. The emission data were collected in the region of 350 to 450 nm using excitation wavelength of 239 nm. XPS data were collected with a CARLO ERBA 1106 instrument. QCM data was collected with the Q-Sense E4 instrument (The authors thank Biolin Scientific AB for offering the Q-Sense E4 instrument).

1.3 *Synthesis of 2,6-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene*

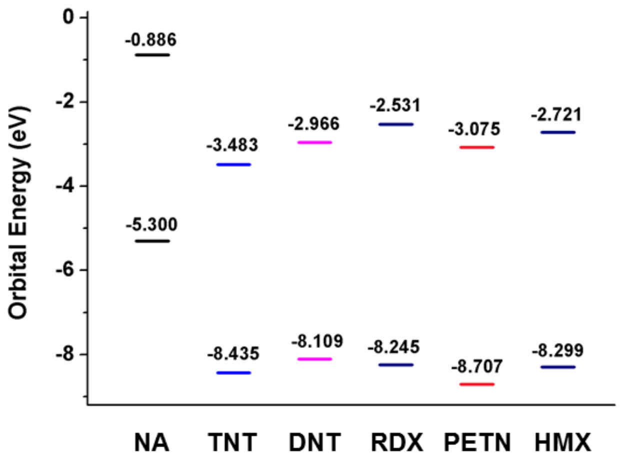


1.4 *Synthesis of 2,6-Bis(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethoxy)naphthalene* (NT) and *2-(2-(2-((6-(2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethoxy)naphtha- lene-2-yl)oxy)ethoxy)ethoxy)ethanol* (NT-1)





Scheme S1. Three-step approach was employed for the construction of CB[8]-based rotaxane structure on solid substrate.



Scheme S2. Band gap energies of the donor (naphthalene NA) and the acceptors (TNT, DNT, PETN, RDX, HMX), which were calculated by using density-functional theory at the B3LYP/6-31G(d) level for the optimized geometries.

Figure S1. The optical figure of the mixture solution with three components: NT, MV^{2+} and CB[8].

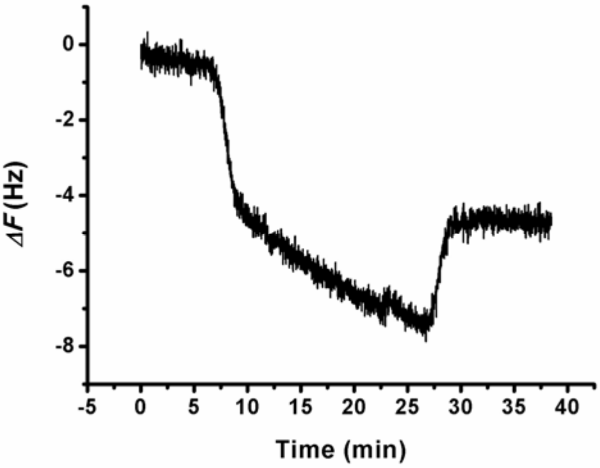


Figure S2. QCM response for the anchoring of the pseudorotaxane CB[8]•NT•MV onto the substrate.

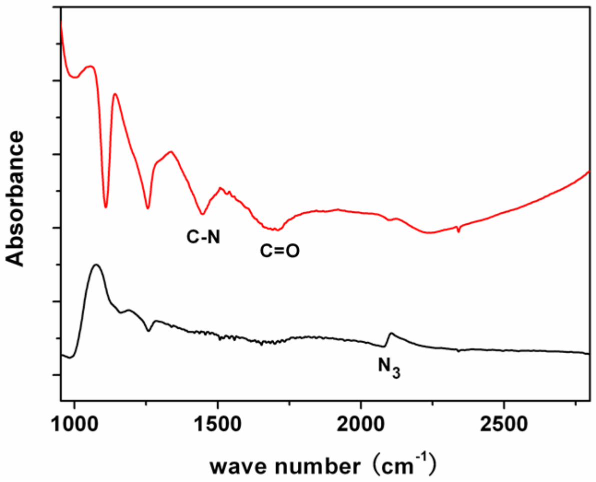


Figure S3. FT-IRTS spectra of the azide-modified wafer before (black line) and after the attachment of the CB[8].NA structure (red line).

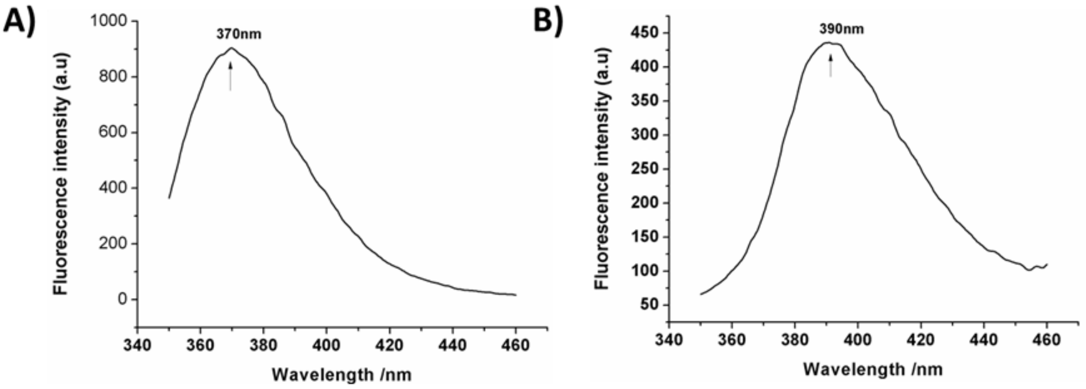


Figure S4. Comparison of the fluorescence emission of (A) in bulky solution and (B) the naphthalene core in the confined nanocavity of CB[8].

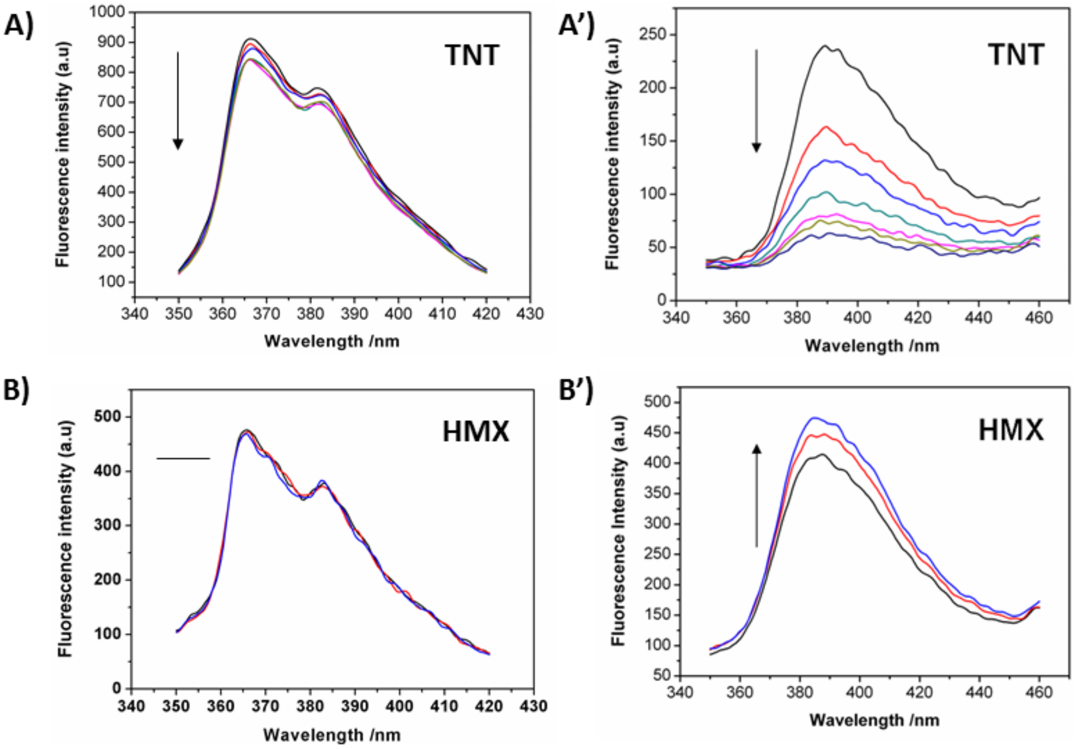


Figure S5. Comparison of the fluorescence response of the naphthalene without (A-B) and with (A'-B') CB[8] upon exposure to explosives.

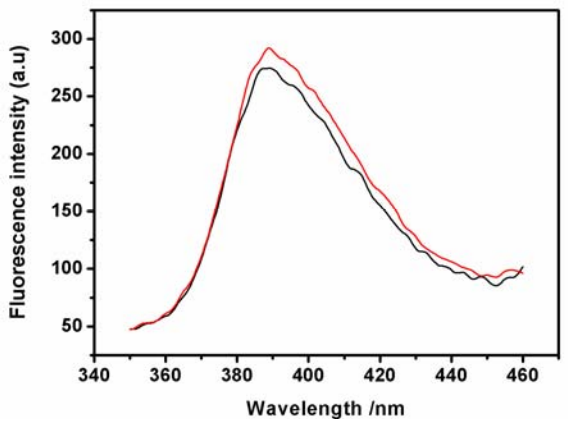


Figure S6. Time-dependent fluorescence intensity of the NT-threaded CB[8] rotaxane on solid substrate upon exposure to TNT (830 ppt) at 0 min (red line), and 1 min (black line).

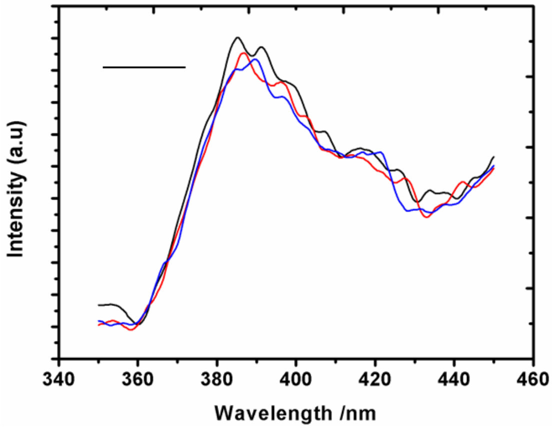


Figure S7. Time-dependent fluorescence intensity of the NT-threaded CB[8] rotaxane on solid substrate upon exposure to saturated vapor (1.3×10^{-19} torr) of naphthalenediimide.

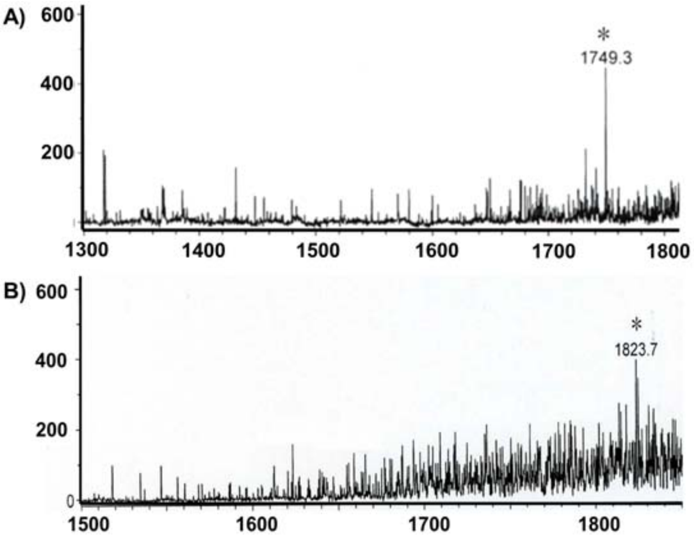


Figure S8. ESI-MS spectrum of the formed CB[8]• 2,6-dihydroxynaphthalene • RDX (A) and HMX (B) host-guest complexes in water.

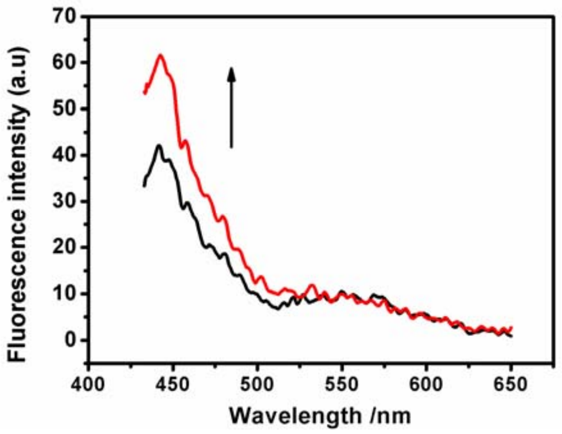


Figure S9. The Time-dependent fluorescence intensity of the ThT-CB[8] film on solid substrate upon exposure to the vapor RDX at 0 min (black line), and 3 min (red line).

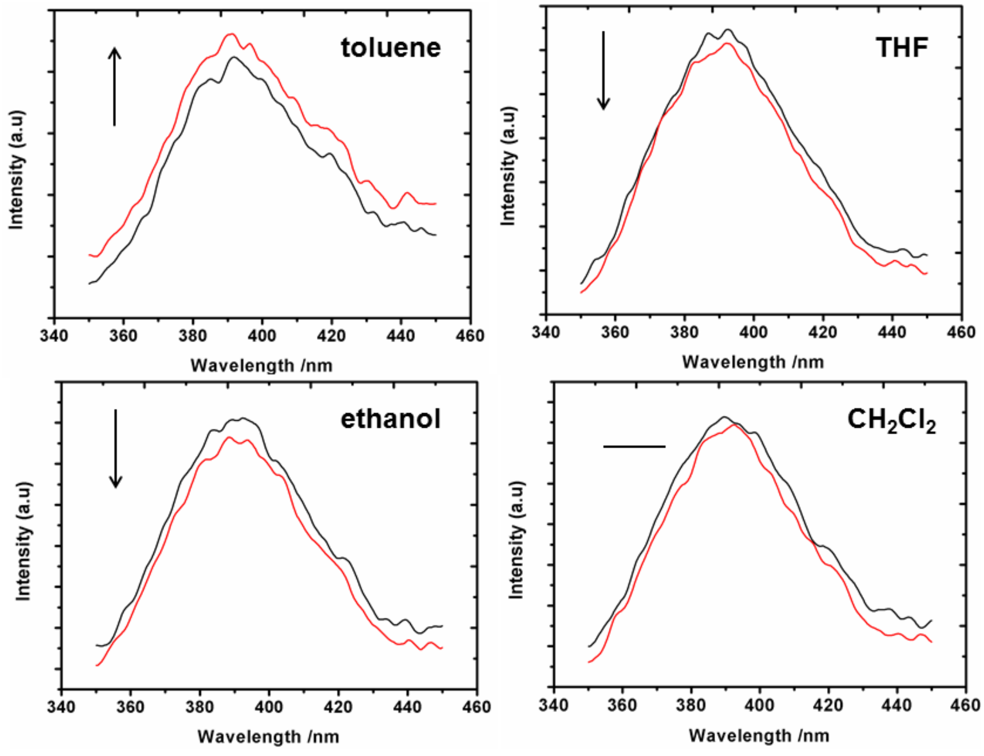


Figure S10. Time-dependent fluorescence intensity of the NT-threaded CB[8] rotaxane on solid substrate upon exposure to saturated vapor of toluene, THF, CH_2Cl_2 and ethanol at 0 min (black line), and 3 min (red line).