Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A cyanide responsive supramolecular nanovalve based on Pd(II)-templated pseudorotaxane

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Supporting Figures:

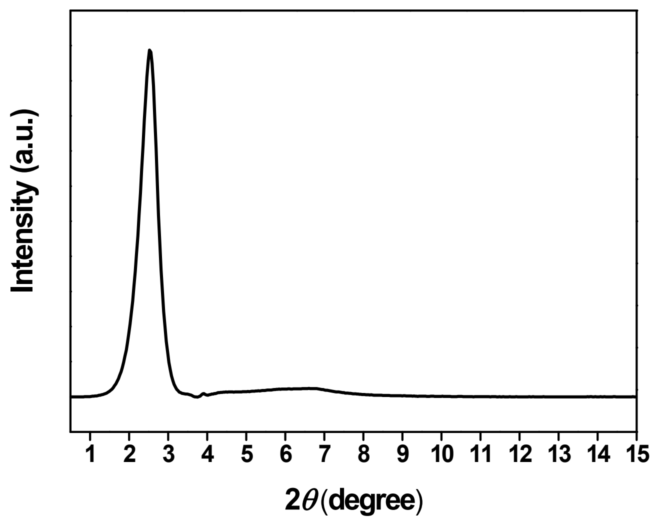


Fig. S1 Small angle Powder XRD of mesoporous silica nanoparticles **MSNs**.

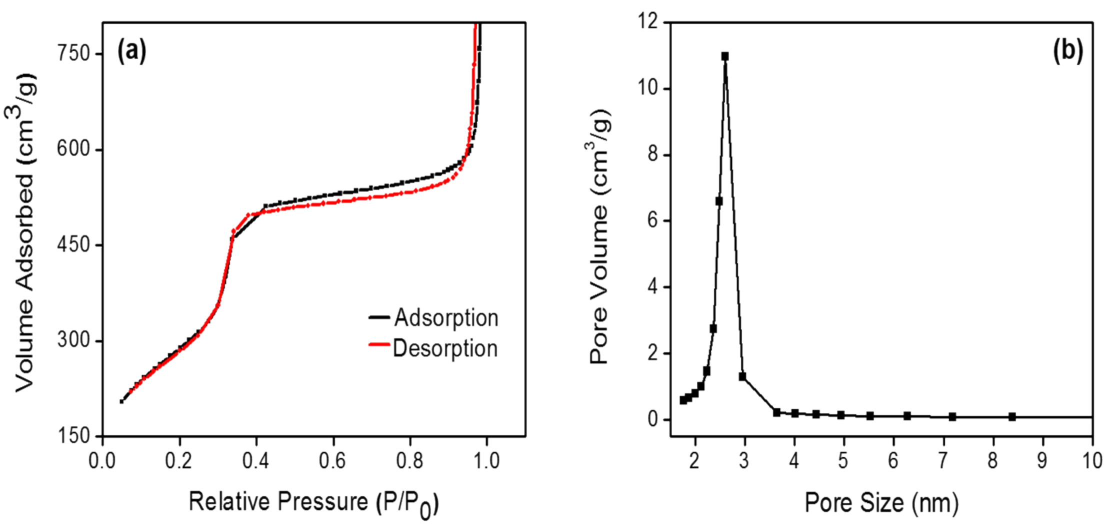


Fig. S2 (a) and (b) N_2 adsorption/desorption isotherms and the corresponding pore size distribution of **MSNs**.

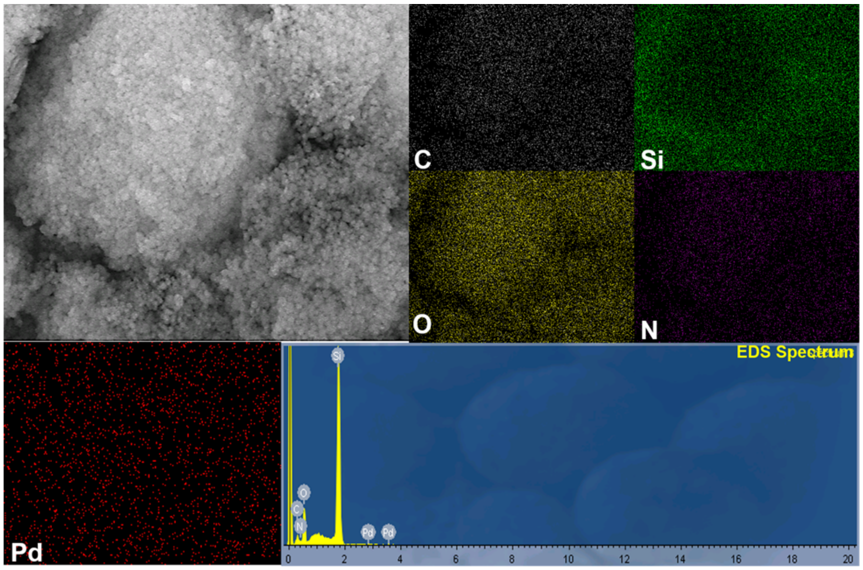


Fig. S3 SEM-EDX analysis and elemental mapping images of nanoparticles **SN3s**

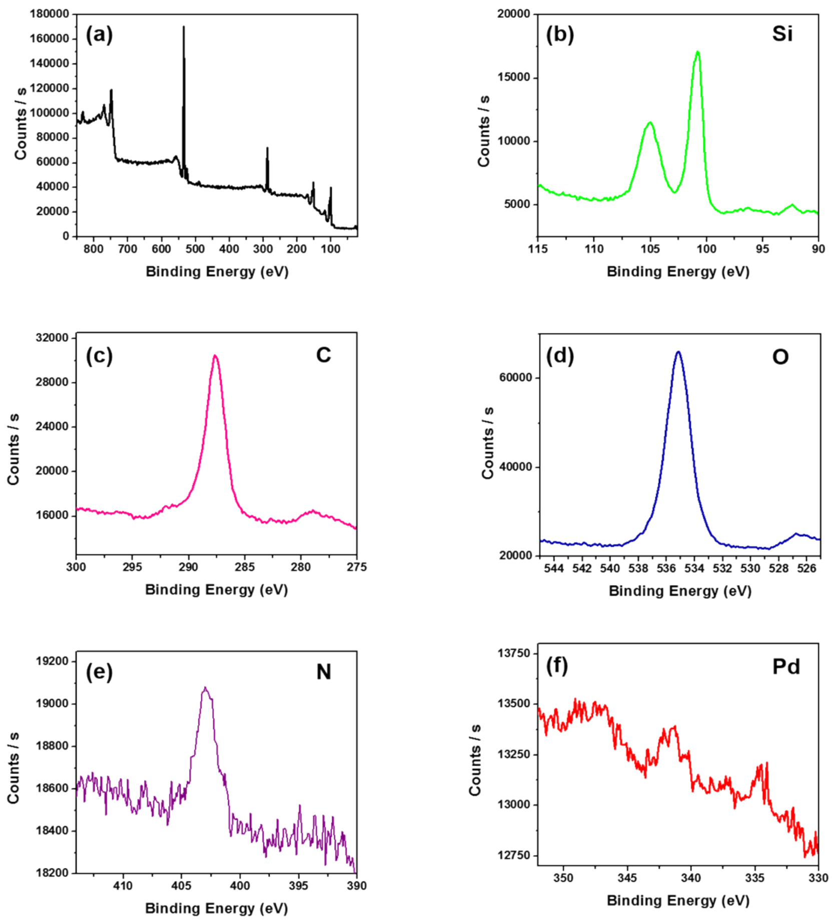


Fig. S4 (a) X-ray photo electron spectroscopy survey scan image of nanoparticles **SN3s**; (b)-(f) photoelectron spectra of Si_{2p}, C_{1s}, O_{1s}, N_{1s} &N_{2p} and Pd ($3d_{3/2}$ & $3d_{5/2}$), respectively.

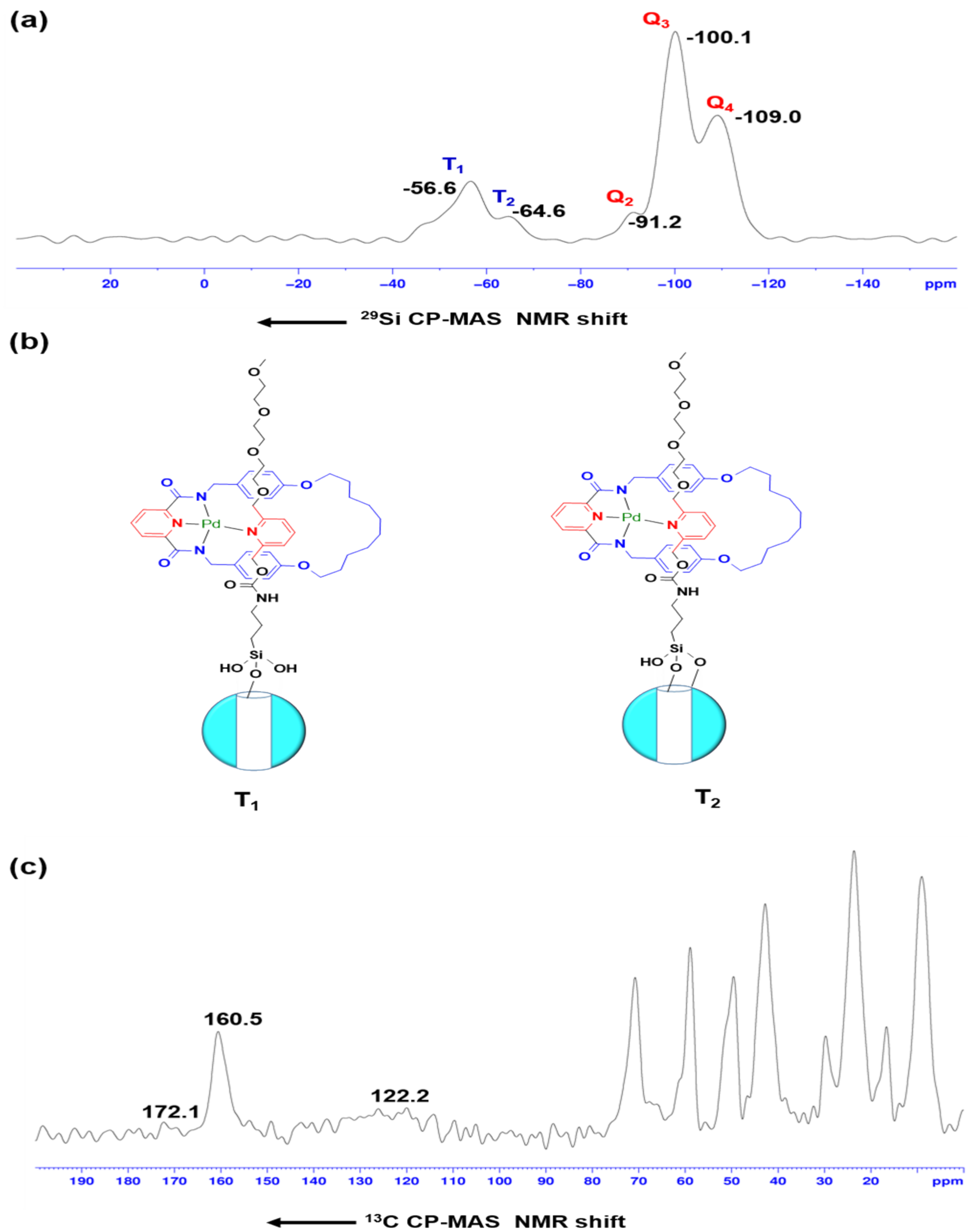


Fig. S5 (a) ^{29}Si CP-MAS NMR spectrum of nanovalve **SN3s**; (b) graphical representation of organic stack functionalized T region and silica Q region; (c) ^{13}C CP-MAS NMR spectrum of nanovalve **SN3s**.

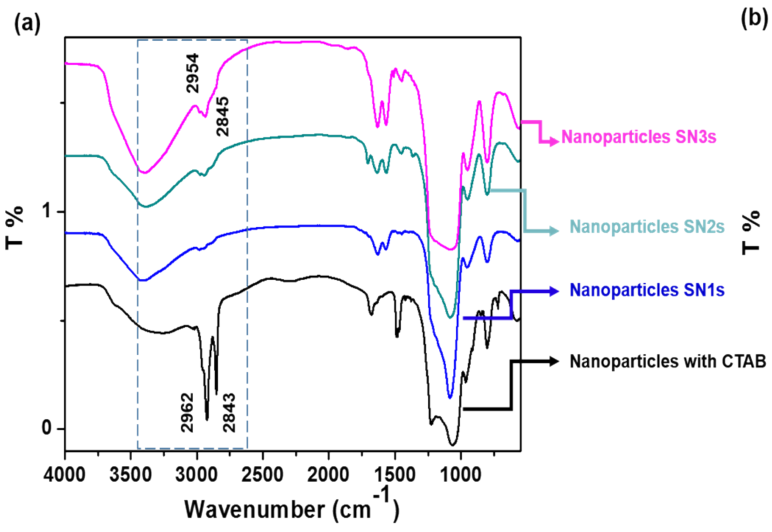


Fig. S6 (a) and (b) IR-chromatogram of whole spectral region and carbonyl, N-H bending regions of CTAB templated, isocyanato linked (**SN1s**), organic stack attached (**SN2s**) and closed with gate (**SN3s**) nanoparticles, respectively.

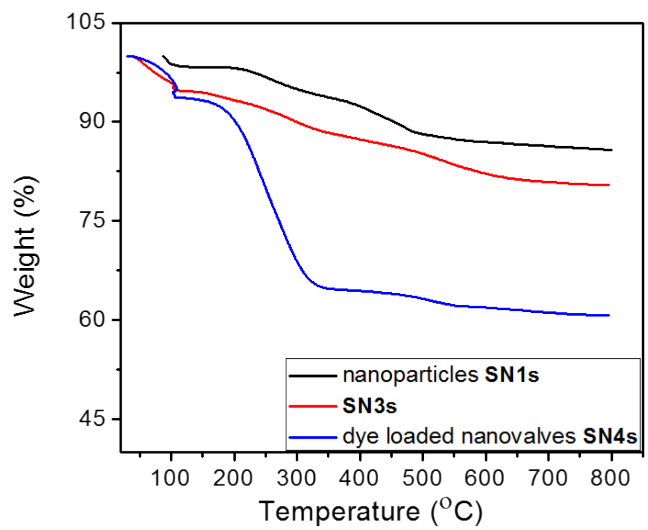


Fig. S7 Thermogravimetric analysis of **SN1s**, **SN3s** and dye loaded nanovalves **SN4s**. The weight losses of **SN1s**, **SN3s** and dye loaded nanovalves **SN4s** from the aforementioned TGA measurements are approximately estimated to be 14.12 %, 19.6 % and 37.60 %, respectively. The corresponding 5.48 % difference in weight losses from bare **SN1s** to gated nanovalves **SN3s** represents the weight loss of pseudorotaxane nanovalves on the surface of **MSNs**, which yields surface density of 0.055 g/g for Pd(II)-templated gate. Likewise, the dye loading capacity (0.180 g/g) is calculated by the weight loss difference between dye loaded nanovalves **SN4s** and **SN3s**.

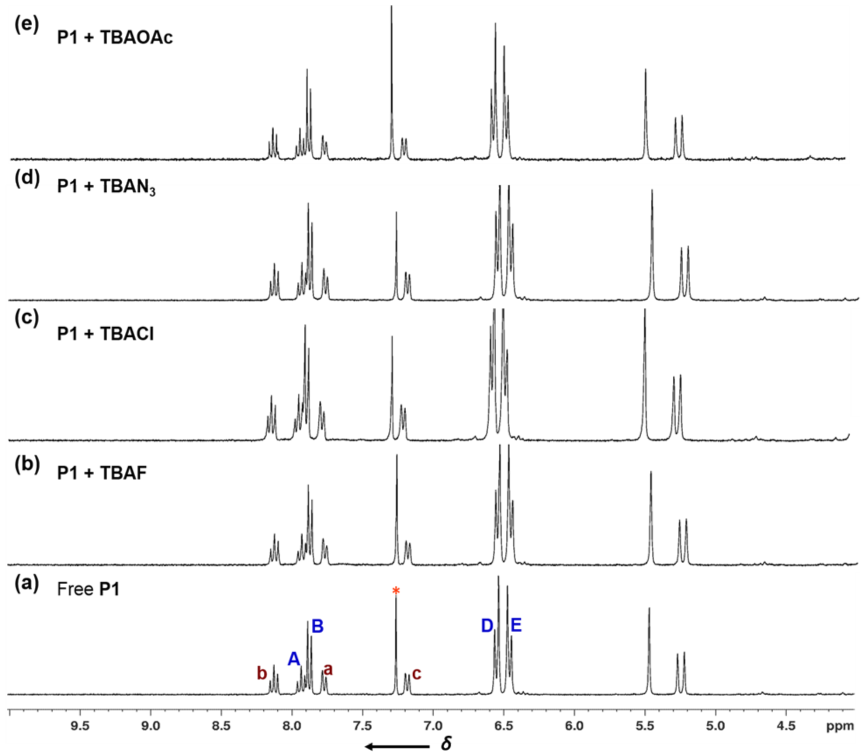


Fig. S8 Changes in [1]H NMR spectra (a-e) ($CDCl_3$, 300 MHz, 25°C) of pseudorotaxane **P1** (3 mM) upon the addition of tetrabutylammonium salts of anions F^-, Cl^-, N_3^- and OAc^- (in CD_3OD, 4 equiv), respectively. The assignments correspond to the lettering shown in main Fig. 1b. The asterisk in this Fig corresponds to $CDCl_3$.

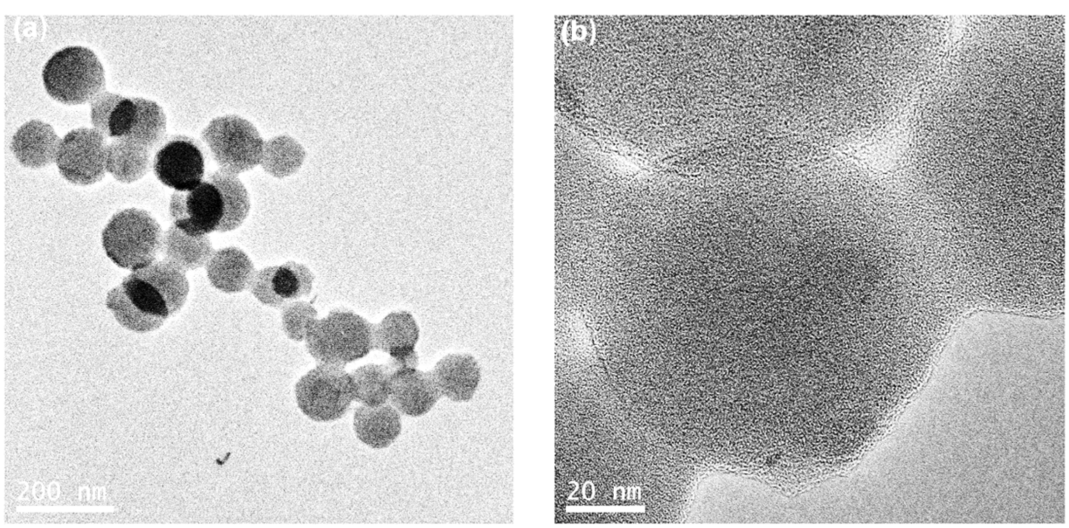
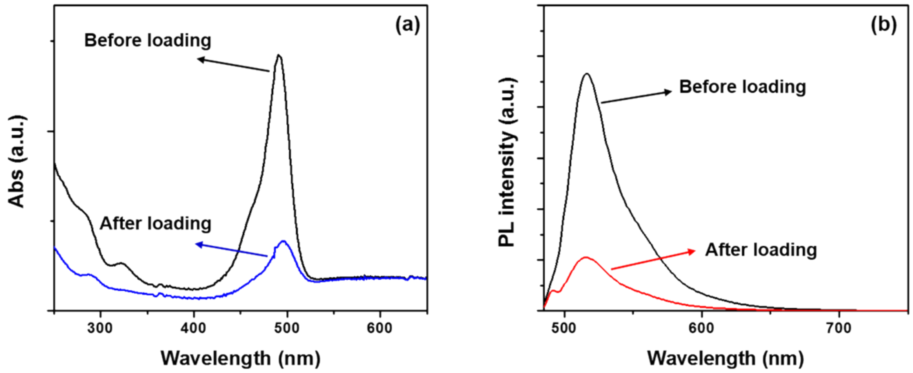


Fig. S9 (a) and (b) HR-TEM micrographs of pore filled Pd(II) metal template gated-nanovalves **SN4s**, enlarged picture in (b) clearly vivifying the guest molecular confinement. Scale bars of (a) and (b) are 200 and 20 nm, respectively.



(c) % of dye loading = $\left(\frac{\text{mass of dye loaded nanovalves - MSNs bare}}{\text{mass of dye}} \right) \times 100$

Fig. S10 (a and b) UV/Vis and PL changes of dye molecule **FDS** before and after loading, respectively; (c) equation utilized for calibrating loading and releasing marvels of **FDS** dye.

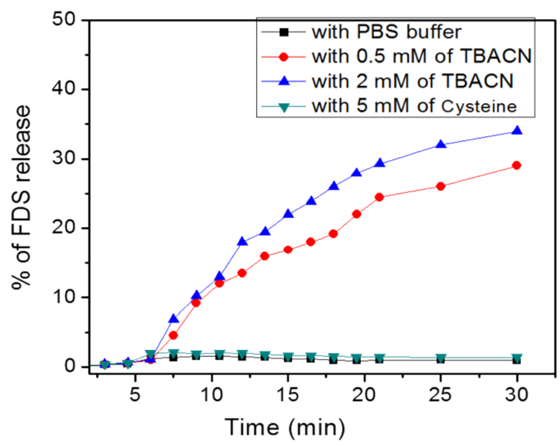


Fig. S11 The **FDS** release profiles of MCM-41 mechanized with Pd(II) metal template gated-nanovalves **SN4s** under cyanide trigger at corresponding concentrations of 0, 0.5 and 2 mM, and in the presence of cysteine 5 mM.

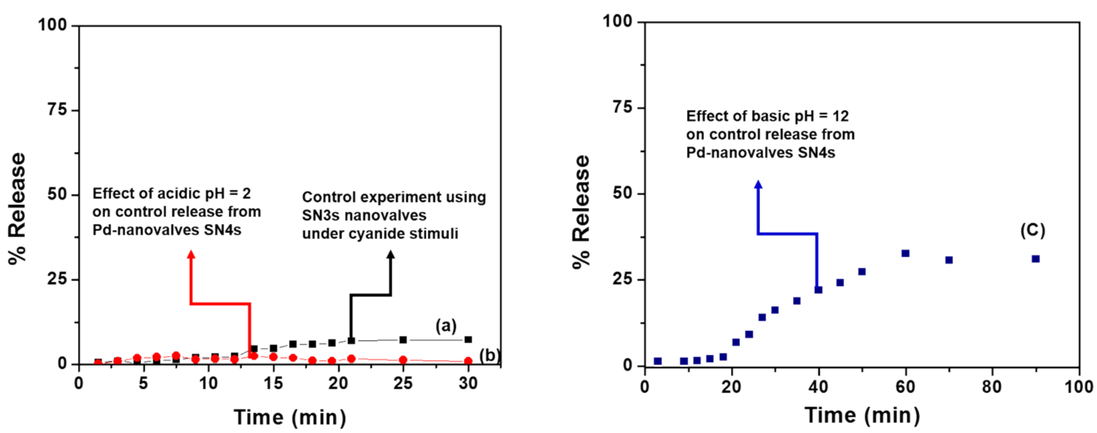


Fig. S12 (a) Control experiment using **SN3s** nanovalves under cyanide stimulus; (b) and c) effect of acidic (pH=2) and basic (pH=12) on control release from Pd-nanovalves **SN4s**, respectively.

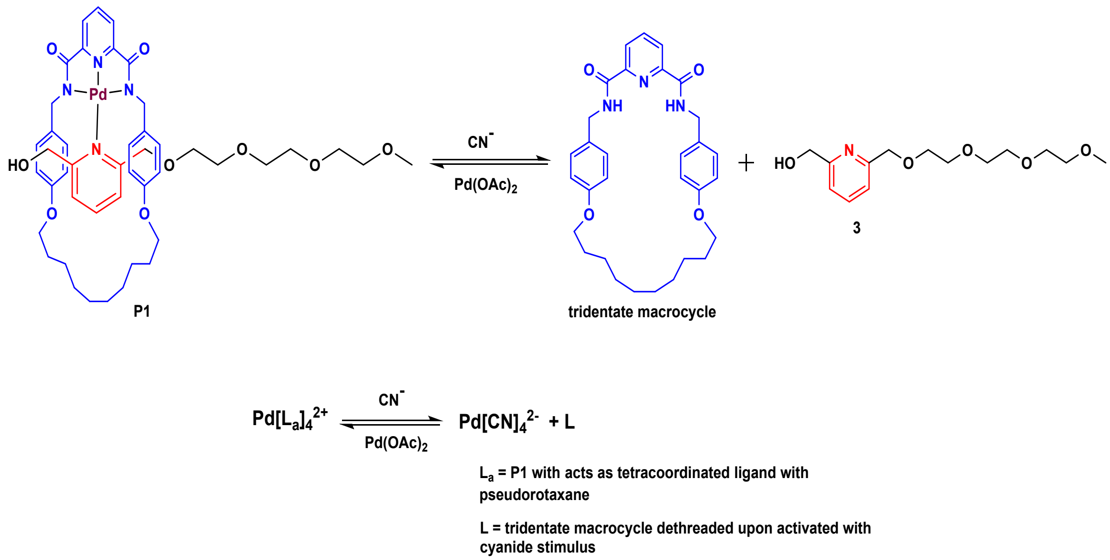
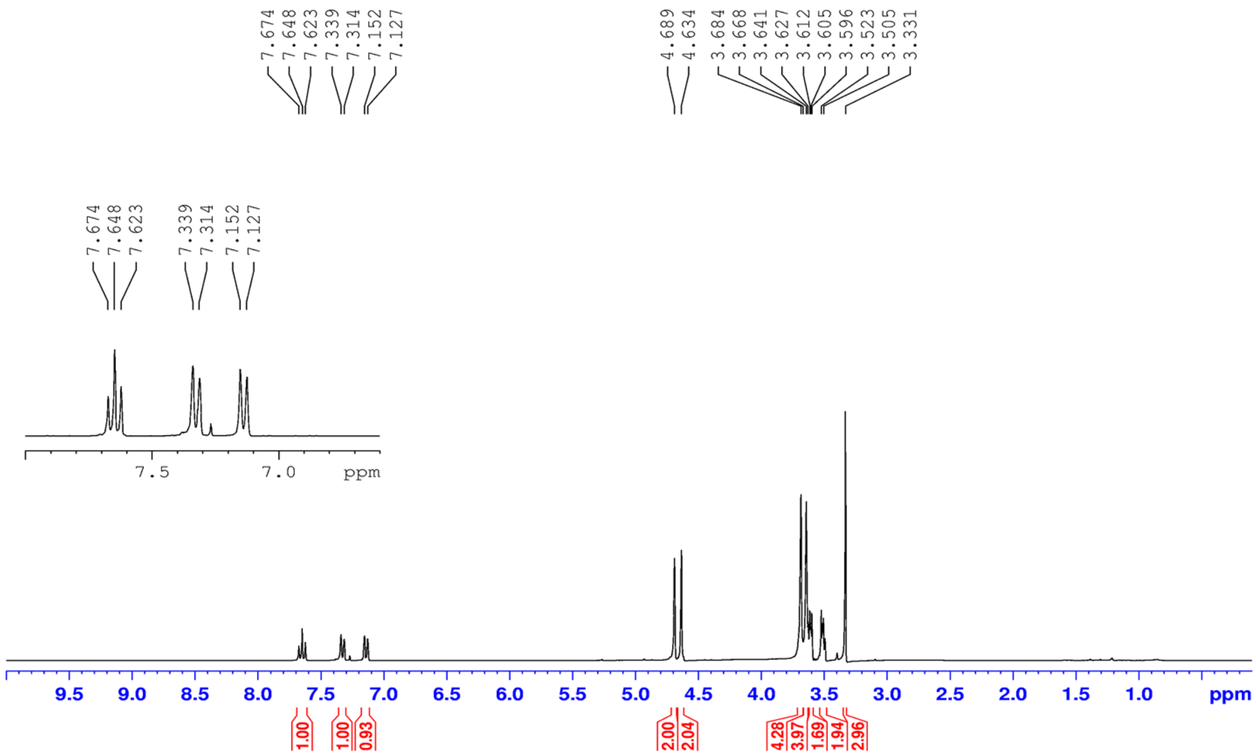


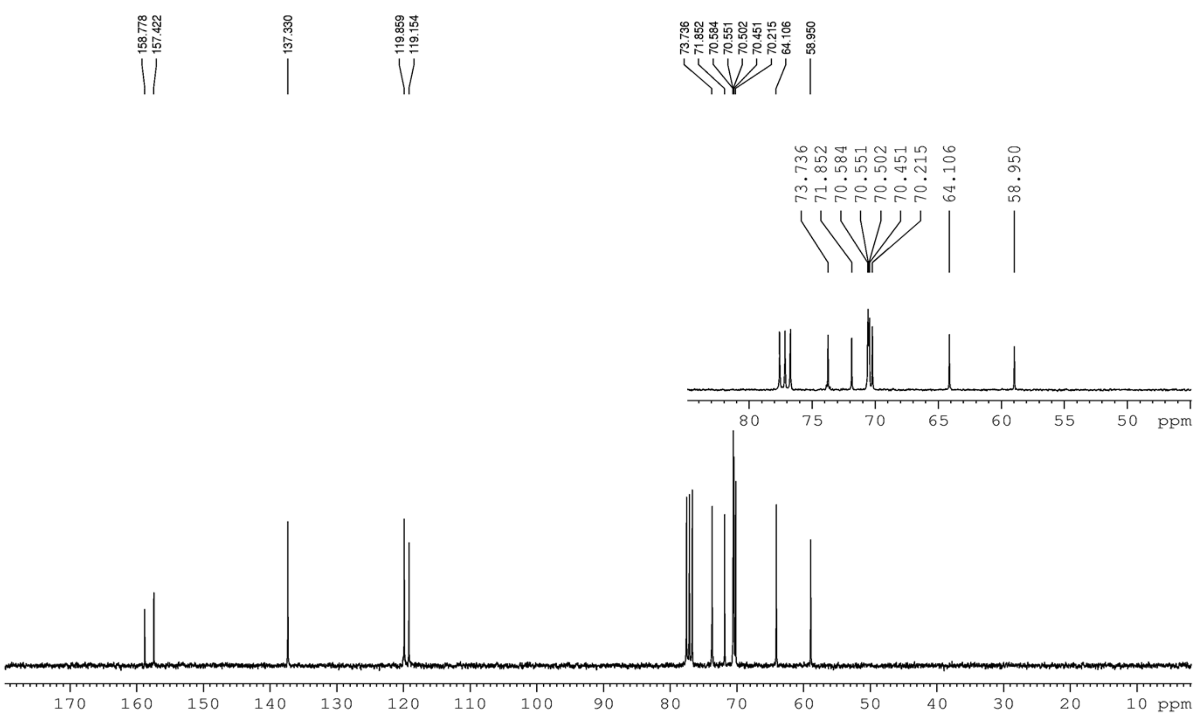
Fig. S13 Plausible working principle and mechanism of Pd(II)-template gated-nanovalves **SN4s** under cyanide trigger

Table S1. N_2 Adsorption-desorption BET analysis surface area, volume and zeta potential values of nanoparticles

Sample	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Zeta potential (mV)	Pore diameter (nm)
MSNs	1155	2.11	- 40.7	2.50
SN1s	1099	1.69	- 10.3	---
SN2s	824	1.31	- 4.3	2.39
SN3s	588	---	32.1	---
SN4s	232	---	---	---

^{1}H (300 MHz) & ^{13}C NMR (75 MHz) spectra of Compound **3**





^{1}H (300 MHz) & ^{13}C NMR (75 MHz) spectra of pseudorotaxane **P1**