Supporting Information

Acid-base controllable nanostructures and fluorescence detection of $H_2PO_4^-$ by molecular shuttling of tetraphenylethene-based [2]rotaxanes

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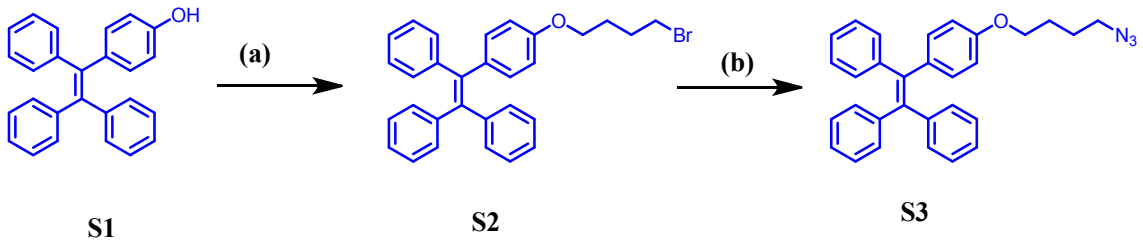
Synthesis overview

The following compounds were synthesized according to the reported procedures: 4-(1,2,2-triphenylvinyl)phenol **S1**[S1] and compound **DBA**.[S2]



Scheme S1. Synthesis of stopper **S3**. Reagents and conditions: (a)1,4 dibromobutane, K_2CO_3, acetone, reflux, 24 h, 79 % (b) NaN_3, DMF, 80 ºC, 12 h, 94%;

Synthetic procedure and characterization

Compound S2

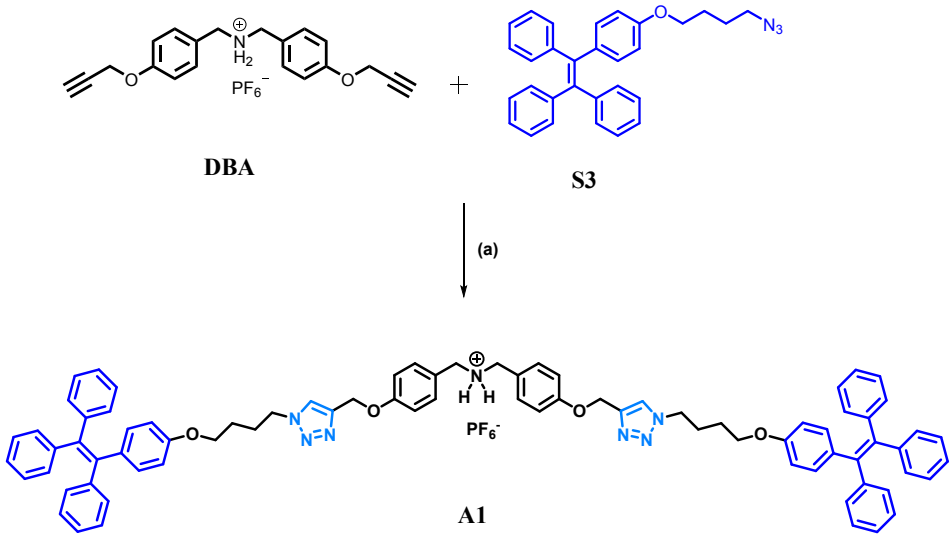
A mixture of **S1** (2.3 g, 6.6 mmol) and K_2CO_3 (4.6 g, 33.3 mmol) in acetone (300 mL) was refluxed under N_2 atmosphere for 1 h, then 1,4-dibromobutane (2 mL, 16.7 mmol) was added into reaction mixture and stirred 24 h. After filtration, the solution was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 1 to 2 % EtOAc in hexane, increase in increments of 0.5 % after 1000 mL of eluent) to afford **S2** as a pale yellow oil (2.5 g, 79 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.13–6.99 (m, 15H), 6.92 (dd, J = 2.1 Hz, 6.9 Hz, 2H), 6.62 (dd, J = 2.1 Hz, 6.6 Hz, 2H), 3.92 (t, J = 6.0 Hz, 2H), 3.47 (t, J = 6.3 Hz, 2H), 2.09–2.00 (m, 2H), 1.95–1.85 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.70, 144.36, 144.30, 140.82, 140.43, 136.52, 132.88, 131.68, 128.05, 127.93, 126.69, 126.57, 113.87, 66.93, 33.84, 29.82, 28.24.

Compound S3

A mixture of **S2** (2.2 g, 4.5 mmol) and NaN_3 (1.48 g, 22.8 mmol) in DMF (15 mL) was stirred at 80 °C for 12 h. After cooling to the room temperature, the reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 3 % EtOAc in hexane) to afford **S3** as a pale yellow

oil (1.9 g, 94 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.13–6.99 (m, 15H), 6.93 (dd, J = 1.8 Hz, 6.9 Hz, 2H), 6.62 (dd, J = 2.1 Hz, 8.7 Hz, 2H), 3.91 (t, J = 5.7 Hz, 2H), 3.35 (t, J = 6.6 Hz, 2H), 1.85–1.75 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.70, 144.35, 144.29, 140.82, 140.42, 136.50, 132.87, 131.67, 128.04, 127.92, 126.67, 126.56, 113.86, 67.27, 51.51, 26.83, 26.08. **HRMS (ESI$^+$)**: m/z = 445.2140 $[M]^+$ (calcd. 445.2154 for $C_{30}H_{27}N_3O$).

Synthesis of thread A1



Scheme S2. Synthesis of thread **A1**. Reagents and conditions: (a) $CuSO_4.5H_2O$, Sodium Ascorbate, THF/water (3:1 ratio), room temp, overnight, 78 %.

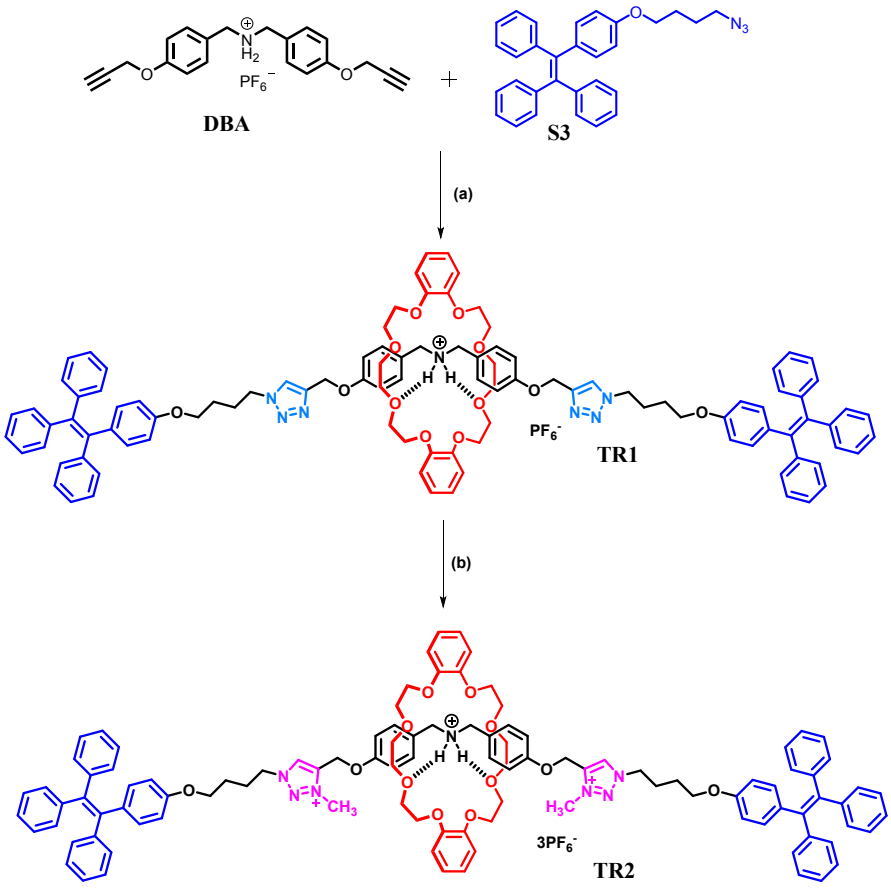
Synthetic procedure and characterization

Thread A1

Compound **DBA** (0.3 g, 0.66 mmol) and **S3** (0.293 g, 0.66 mmol) were dissolved in THF/H_2O (v/v = 3:1, 40 mL) in a round-bottomed flask under an inert atmosphere. An aqueous solution of copper (II) sulphate pentahydrate (0.328 g, 1.32 mmol) and sodium ascorbate (0.522 g, 2.64 mmol) was added to the reaction mixture and allowed to stir at room temperature for overnight. Completion of the reaction was monitored by TLC (SiO_2). The solvent was removed under reduce pressure and the crude product dissolved in DCM (100 mL). The organic phase was washed successively with an aqueous solution of NH_4Cl (2 × 30 mL) and H_2O (30 mL) and was separated, dried ($MgSO_4$) and evaporated. The crude product was purified by silica gel chromatography (DCM / MeOH, 9.8/0.2) to afford the pure compound **A1** as a pale white solid

in 78 % yield. **^{1}H NMR** (400 MHz, CD_3CN): δ_H 7.83 (s, 2H), 7.27 (d, J = 8.08 Hz, 4H), 7.13–7.11 (m, 14H) 7.05–7.03 (m, 15H), 6.97 (d, J = 8.52, 4H) 6.92 (d, J = 8.84, 4H) 6.65–6.63 (m, 4H), 5.14 (s, 4H), 4.43–4.39 (m, 4H), 3.90–3.87 (m,4H). 3.70 (s, 4H), 2.03–1.96 (m, 4H), 1.72–1.65 (m, 4H) ppm; **^{13}C NMR** (100 MHz, CD_3CN) δ (ppm) = 157.51, 144.01, 143.95, 140.68, 140.29, 135.98, 132.13, 130.93, 130.89, 130.86, 127.75, 127.67, 126.40, 126.34, 126.30, 123.67, 113.38, 66.92, 61.54, 49.63, 26.71, 25.87. **HRMS–ESI** (m/z): $[M–PF_6^-]^+$ calcd for $C_{80}H_{74}N_7O_4^+$, 1196.5797; found, 1196.5803.

Synthesis of [2]rotaxane TR1 and TR2



Scheme S3. Synthesis of [2]rotaxane **TR1** and **TR2**. Reagents and condition s: (a) $Cu(CH_3CN)_4PF_6$, 2,6-lutidine, dry DCM, under N_2 atmosphere, room temperature, 24 h, 75%; (b) CH_3I, CH_3CN, NH_4PF_6, 40 ºC, 4 d, 84%.

Synthetic procedure and characterization

[2]Rotaxane TR1

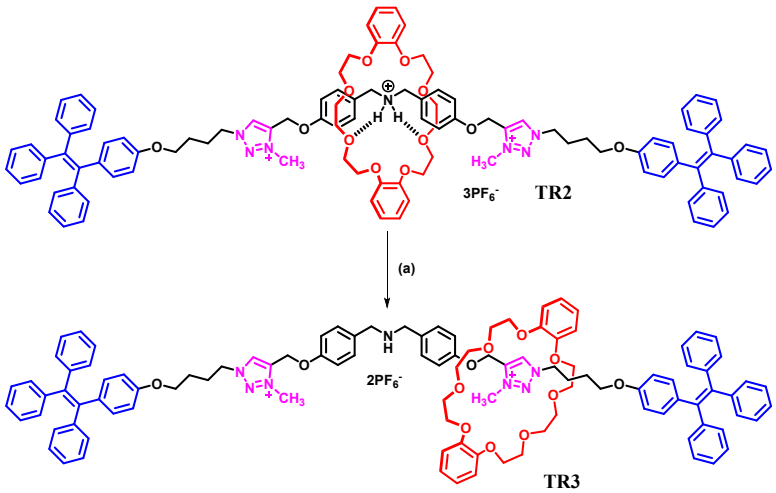
To a solution of **DBA** (500 mg, 1.11 mmol), **DB24C8** (646 mg, 1.44 mmol) in degassed DCM (50 mL) was stirred at room temperature for 2 h under N_2 atmosphere. Then, a solution of **S3** (988 mg, 2.22 mmol) in DCM (10 mL), $Cu(CH_3CN)_4PF_6$ (1.65 g, 4.43 mmol) and 2,6-lutidine (40 μL, 0.35 mmol) were added. The reaction mixture was stirred for 24 h at room temperature. The resulting mixture was dissolved by DCM and then washed with brine three times. Then the organic phase was dried over anhydrous magnesium sulfate, and concentrated which was purified by column chromatography over silica gel (eluent: 0 to 2 % MeOH in DCM, increase in increments of 0.5 % after 750 mL of eluent) to afford [2]rotaxane **TR1** as a pale white solid (1.5 g, 75 %). **^{1}H NMR** (400 MHz, ACN-d_3): δ_H 7.81 (s, 2H), 7.41 (br, 2H), 7.28 (d, J = 8.72 Hz, 4H), 7.15–7.11 (m,18H), 7.06–7.01 (m, 12H), 6.93 (d, J = 8.8 Hz, 4H), 6.89–6.86 (m, 4H), 6.83–6.78 (m, 8H), 6.65 (d, J = 8.84 Hz, 4H), 5.04 (s, 4H), 4.59 (t, J = 6.64 Hz, 4H), 4.42 (t, J = 7.04 Hz, 4H), 4.29–4.27 (m, 4H), 4.07–4.05 (m, 4H), 3.90 (t, J = 6.24 Hz, 4H), 3.78–3.75 (m, 8H), 3.63 (s, 4H), 3.58 (s, 4.26), 2.03–1.95 (m, 4H), 1.73–1.66 (m, 4H) ppm; **^{13}C NMR** (75 MHz, ACN-d_3): δ = 159.7, 158.5, 149.4, 148.4, 145.0, 144.9, 141.6, 141.3, 137.0, 133.1, 131.8, 128.7, 128.6, 127.4, 127.3, 125.5, 123.6, 122.2, 116.8, 115.6, 114.5, 113.4, 71.5, 71.1, 69.4, 68.8, 67.9, 62.3, 52.7, 50.6, 27.7, 26.9. **HRMS (ESI$^+$)**: m/z = 1644.7784 $[M–PF_6]^+$ (calcd. 1644.7899 for $C_{104}H_{106}N_7O_{12}$).

[2]Rotaxane TR2

To a solution of [2]rotaxane **TR1** (1 g, 0.56 mmol) in MeCN (15 mL), CH_3I (15 mL) was added to the reaction mixture. The reaction mixture was heated at 40 °C for 4 days. Then, the solvent was removed under reduced pressure and the crude product was dissolved in acetone (15 mL) and DCM (15 mL), a saturated aqueous solution of NH_4PF_6 was added and the mixture was stirred for 24 hours at room temperature. The resulting mixture was dissolved by DCM and then washed with brine three times. Then the organic phase was dried over anhydrous magnesium sulfate, and concentrated which was purified by column chromatography over silica gel (eluent: 0 to 2 % MeOH in DCM, increase in increments of 0.5 % after 750 mL of eluent) to afford [2]rotaxane **TR2** as a pale brown solid (1 g, 84 %). **^{1}H NMR** (400 MHz, ACN–d_3): δ_H = 8.43 (s, 2H), 7.50 (br, 2H), 7.36 (d, J = 8.72 Hz, 4H), 7.16–7.10 (m, 18H), 7.08–7.01 (m, 12H), 6.95 (d,

J = 8.8 Hz, 4H), 6.87 (m, 12H), 6.69 (d, J = 8.8 Hz, 4H), 5.15 (s, 4H), 4.66 (m, 8H), 4.22 (s, 6H), 4.07 (m, 4H), 3.95 (t, J = 6.12 Hz, 4H), 3.82–3.79 (m,10H), 3.67 (s, 4H), 3.66 (s, 4H), 2.15–2.13 (m, 4H), 1.83–1.79 (m, 4H) ppm; **^{13}C NMR** (75 MHz, ACN–d_3): δ = 158.5, 158.4, 149.7, 148.4, 145.1, 145.0, 144.9, 141.6, 141.5, 140.5, 137.2, 133.2, 132.2, 131.9, 130.4, 128.8, 128.7, 127.5, 127.4, 126.9, 122.7, 122.2, 115.6, 115.4, 114.6, 113.4, 71.6, 71.8, 70.2, 69.5, 68.8, 67.7, 59.0, 54.7, 52.6, 39.4, 26.9. **HRMS (ESI$^+$):** m/z = 1819.7760 $[M–2PF_6]^+$ (calcd. 1819.8011 for $C_{106}H_{112}F_6N_7O_{12}P$).

Synthesis of [2]rotaxane TR3



Scheme S4. Synthesis of [2]rotaxane **TR3** with reagents and conditions: (a) DCM, aq. NaOH (0.1M), 2 h, 95%.

Synthetic procedure and characterization

[2]Rotaxane TR3

[2]Rotaxane **TR2** (50 mg, 23.69 mmol) was dissolved in dichloromethane (5 mL). NaOH (aq) 1 M (2 mL) was added and the mixture was stirred vigorously at room temperature for 2 h. The layers were separated, the organic phase dried over $MgSO_4$, filtered off and concentrated affording the rotaxane [2]rotaxane **TR3** (40 mg, 95%) as a pale brown solid. **^{1}H NMR** (300 MHz, ACN-d_3): δ = 9.07 (s,1H), 8.44 (s, 1H), 7.32 (d, J = 8.4 Hz, 4H), 7.14–7.09 (m, 18H), 7.05–6.99 (m, 12H), 6.86 (d, J = 8.4 Hz, 6H), 6.83–6.63 (m, 10H), 6.56 (br, 4H), 5.01 (br, 2H), 4.96 (br, 2H), 4.90 (br, 4H), 4.19 (t, J = 4.5 Hz, 4H), 3.97 (s, 6H), 3.76 (t, J = 4.5 Hz, 6H), 3.69 (s, 12H), 3.64 (s, 4H), 3.53 (br, 6H), 2.20 (br, 4H), 1.77–1.73 (m, 4H). **^{13}C NMR** (75

MHz, ACN–d_3): δ = 157.4, 156.0, 148.5, 147.6, 144.0, 143.9, 140.6, 140.3, 136.0, 134.9, 132.1, 130.8, 130.0, 129.4, 127.7, 127.6, 126.4, 124.1, 122.3, 121.3, 120.8, 118.7, 115.4, 114.6, 113.5, 70.7, 69.7, 68.9, 68.6, 68.3, 67.9, 58.1, 53.5, 51.9, 31.3, 29.5, 25.5, 22.3, 13.3. **HRMS (ESI$^+$):** *m/z* = 1964.7647 $[M+H]^+$ (calcd. 1964.7653 for $C_{106}H_{112}F_{12}N_7O_{12}P_2$).

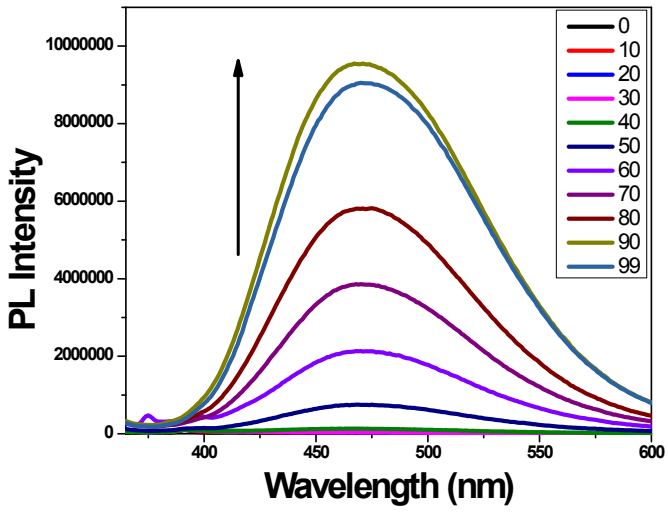


Fig. S1 Fluorescence spectra of thread **A1** (10μM) with different water fractions (λ_{ex} = 325 nm) in CH_3CN/water solutions.

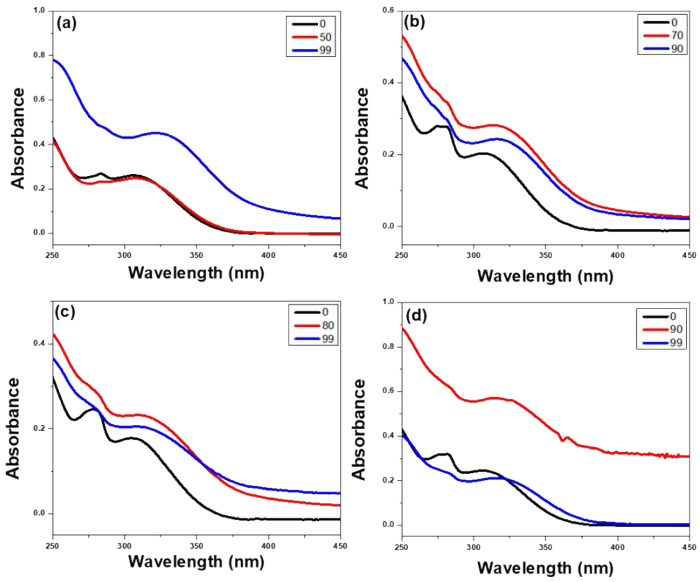


Fig. S2 UV-vis absorption spectra (10μM) with different water fractions in CH_3CN/water solutions; (a) thread **A1** (b) [2]rotaxane **TR1** (c) [2]rotaxane **TR2** and (d) [2]rotaxane **TR3**.

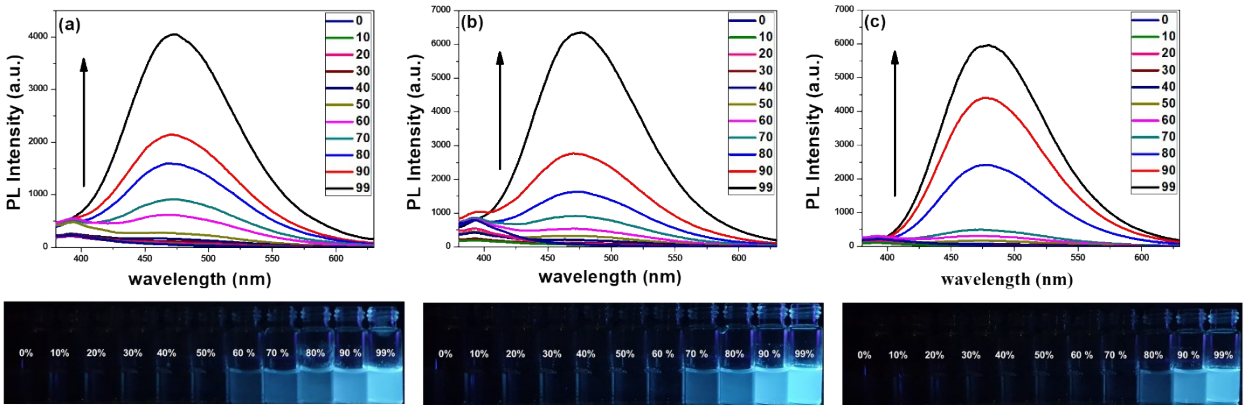


Fig. S3 Fluorescence emission spectra and photographs of [2]rotaxanes (a) **TR1**, (b) **TR2** and (c) **TR3** (10 μM) in DMSO/glycerol solutions with different glycerol fractions (λ_{ex} = 325 nm). Insets: Photo images of fluorescence emissions (excited by UV lamp at 365 nm).

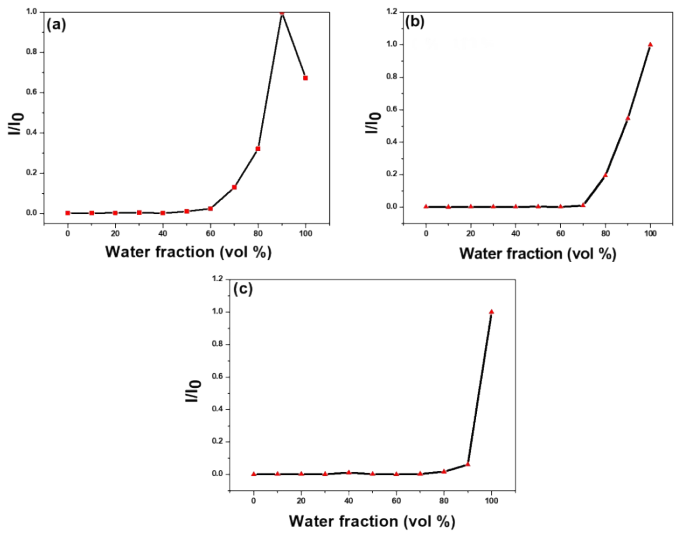


Fig. S4 PL Plots of I/I_0 versus water fractions (f_w) of [2]rotaxanes (a) **TR1**, (b) **TR2** and (c) **TR3**. Where I_0 = emission intensity in pure CH_3CN solution (10μM).

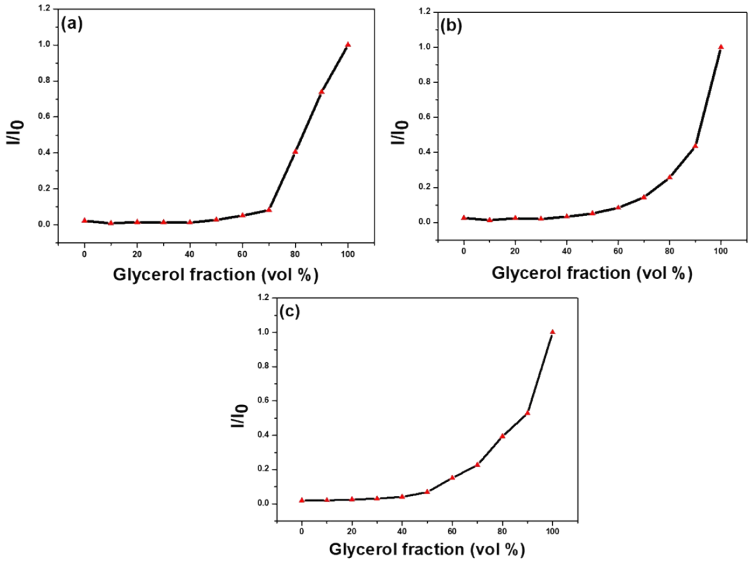


Fig. S5 PL Plots of I/I_0 versus glycerol fractions (f_w) of [2]rotaxanes (a) **TR1**, (b) **TR2** and (c) **TR3**. Where I_0 = emission intensity in pure DMSO solution (10μM).

Table S1. Time-resolved fluorescence decay constants of [2]rotaxanes **TR1**, **TR2** and **TR3** in pure CH_3CN solvent and at 90% of water fraction (f_w) in the CH_3CN/water solutions.

Compounds	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{Avg} (ns)
TR1 (0%)	4.378	1.0300	57.1	49.29	1.13
TR1 (90%)	1.134	0.6907	77.38	22.62	2.72
TR2 (0%)	4.964	1.4243	45.74	54.26	1.64
TR2 (90%)	0.683	2.5903	49.82	50.18	3.04
TR3 (0%)	1.370	5.502	41.40	58.60	3.79
TR3 (90%)	2.712	0.7349	56.75	43.25	3.79

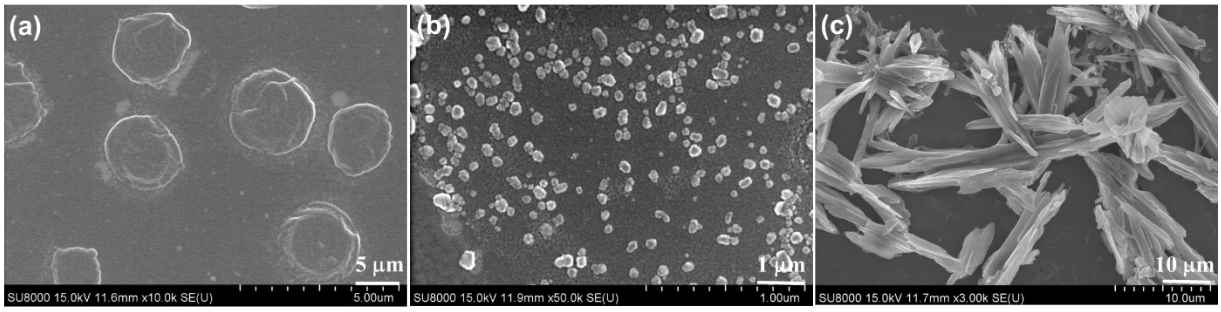


Fig. S6 FE-SEM images of thread **A1** (1.0 µM): (a) in CH_3CN only, (b) CH_3CN/water (f_w = 50%) (c) CH_3CN/water (f_w = 90%). Scale bar was a = 5 µm, b = 1µm and c = 10 µm.

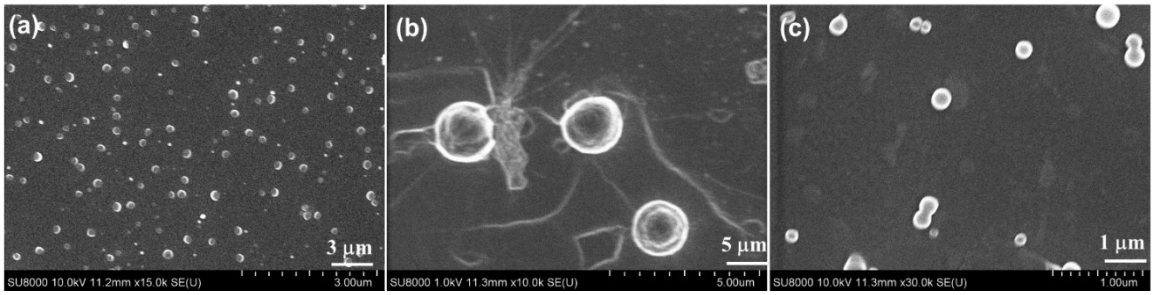


Fig. S7 FE-SEM images of [2]rotaxanes in CH_3CN (1.0 μM) (a) **TR1**, (b) **TR2** and (c) **TR3** Scale bar was a = 3 μm, b = 5μm and c = 1 μm.

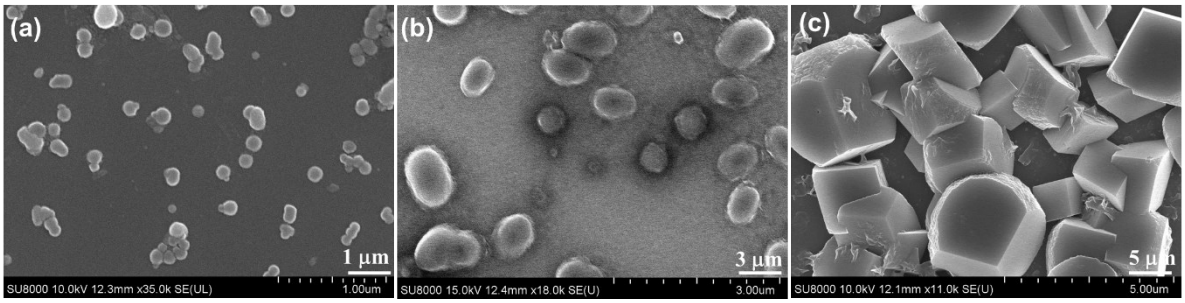


Fig. S8 FE-SEM images of [2]rotaxanes in CH_3CN/water solutions (1.0 μM): (a) 70% f_w of **TR1**, (b) 80% f_w of **TR2**, (c) 90% f_w of **TR3**. Scale bar is 1 μm for Figs a while it is 3 μm and 5 μm in Figs b and c, respectively.

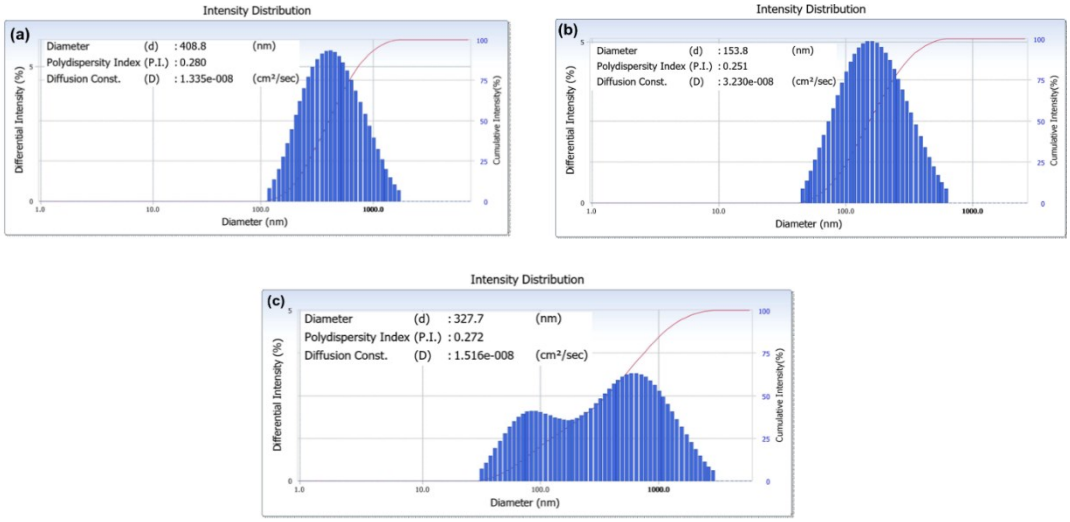


Fig. S9 The size distributions of [2]rotaxanes (a) **TR1** at 90 % f_w, (b) **TR2** at 99 % f_w and (c) **TR3** at 99 % f_w in CH_3CN/water solutions (1.0 μM).

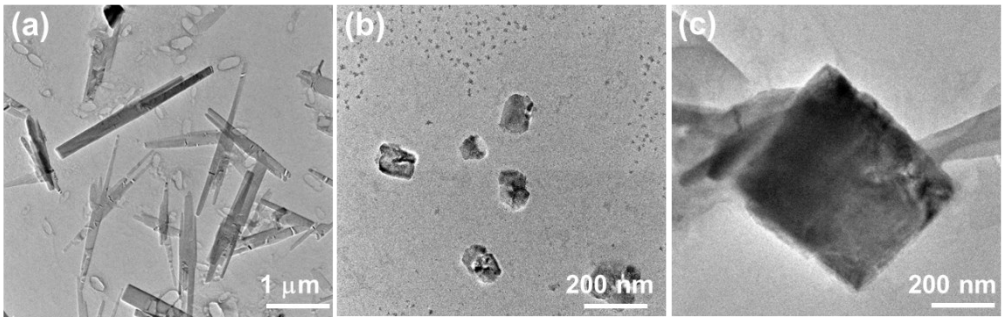


Fig. S10 TEM images of [2]rotaxanes in CH_3CN/water solutions (1.0 μM): (a) 90% f_w of **TR1**, (nanorods) (b) 90% f_w of **TR3**, (truncated cubes) and (c) 99% f_w of **TR3** (nanocube) . Scale bar is 1 μm for Figs a = μm, b and c = 200 nm.

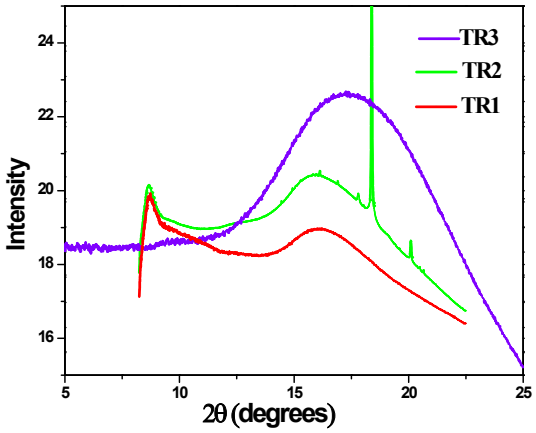


Fig. S11 Powder XRD patterns of [2]rotaxanes **TR1**, **TR2** and **TR3**.

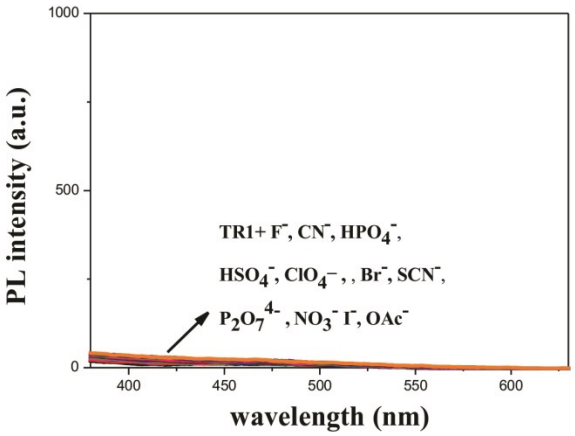


Fig. S12 Fluorescence spectra of [2]rotaxane **TR1** (10 μM) in the presence of various TBA salts in CH_3CN solution (10 μM).

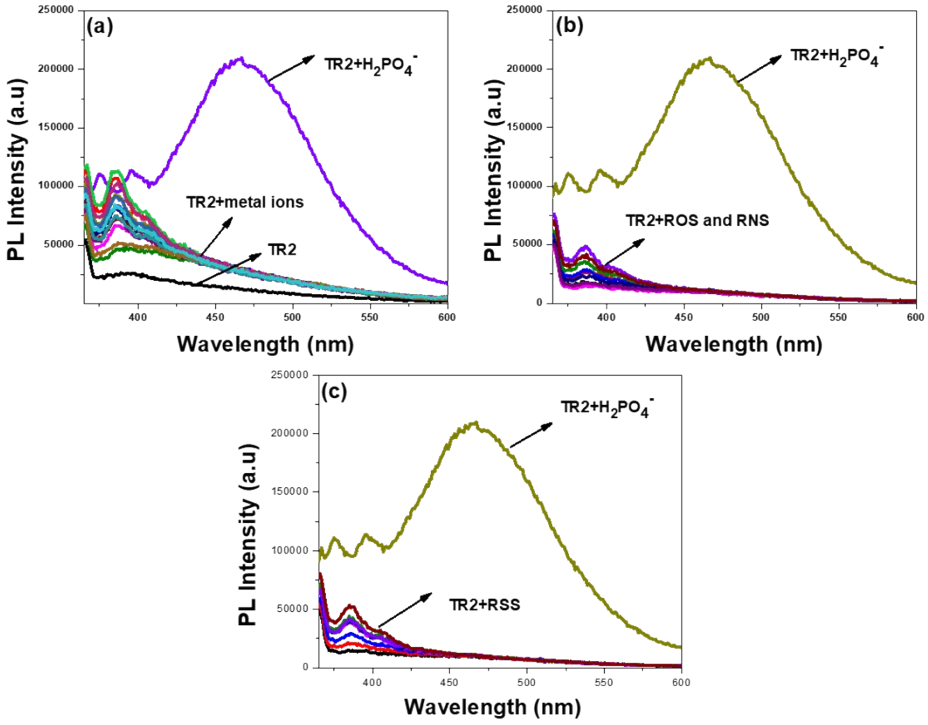


Fig. S13 Fluorescence spectra of [2]rotaxane **TR2** (10 μM) in the presence of (a) metal ions, (b) ROS & RNS and (c) RSS in CH_3CN solutions in contrast to $H_2PO_4^-$.

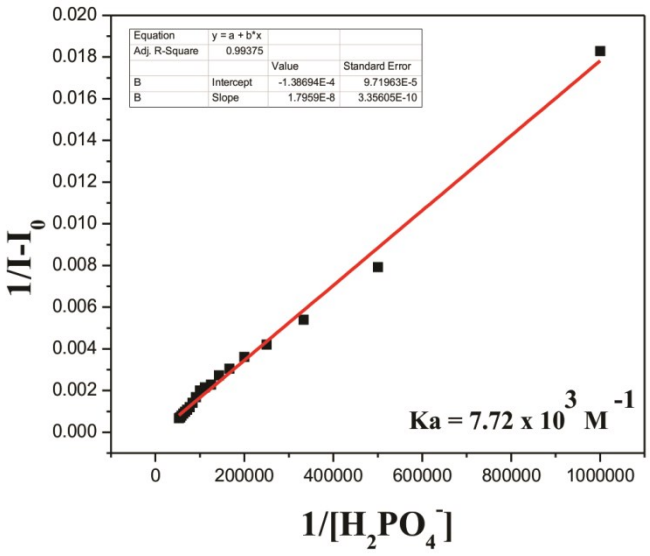


Fig. S14 Binding constant of [2]rotaxane **TR2** for the titration of $H_2PO_4^-$ against the ratio of fluorescence response for chemosensor in CH_3CN (10 μM).

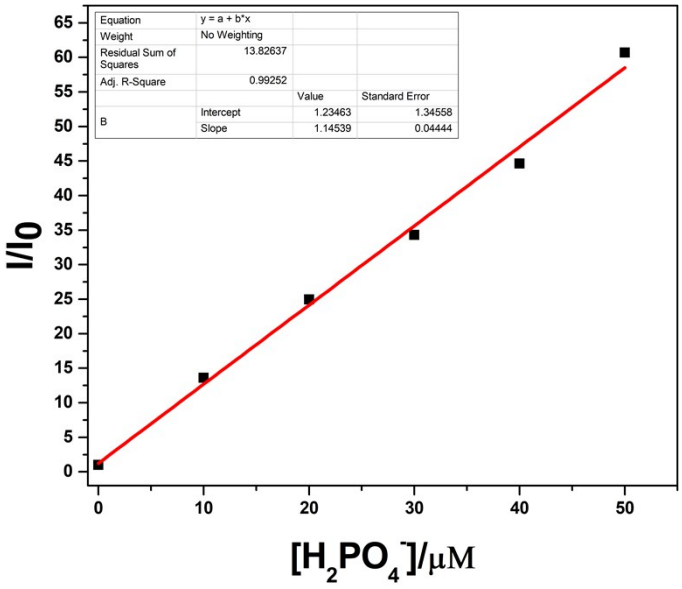


Fig. S15 Detection limit of [2]rotaxane **TR2** in CH_3CN (10 μM) upon increasing concentrations of $H_2PO_4^-$.

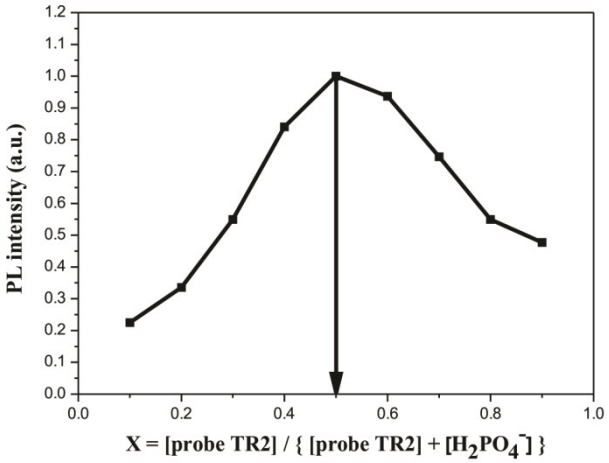


Fig. S16 Job's plots of complexes [2]rotaxane **TR2-$H_2PO_4^-$** in CH_3CN. The total concentration of [2]rotaxane **TR2** and **$H_2PO_4^-$** was 50.0 μM. The monitored wavelength was 480 nm.

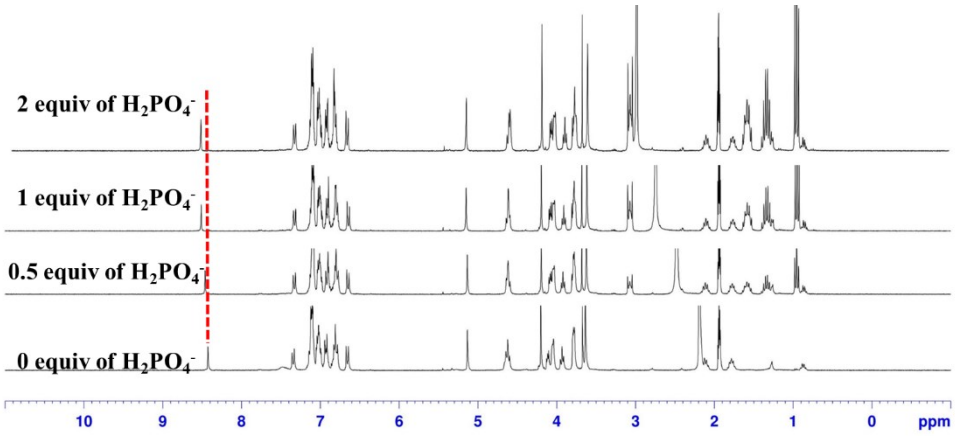


Fig. S17 ^{1}H **NMR** spectra of compound [2]rotaxane **TR2** (10 mM) in the presence of TBA-$H_2PO_4^-$ in D_2O/CH_3CN.

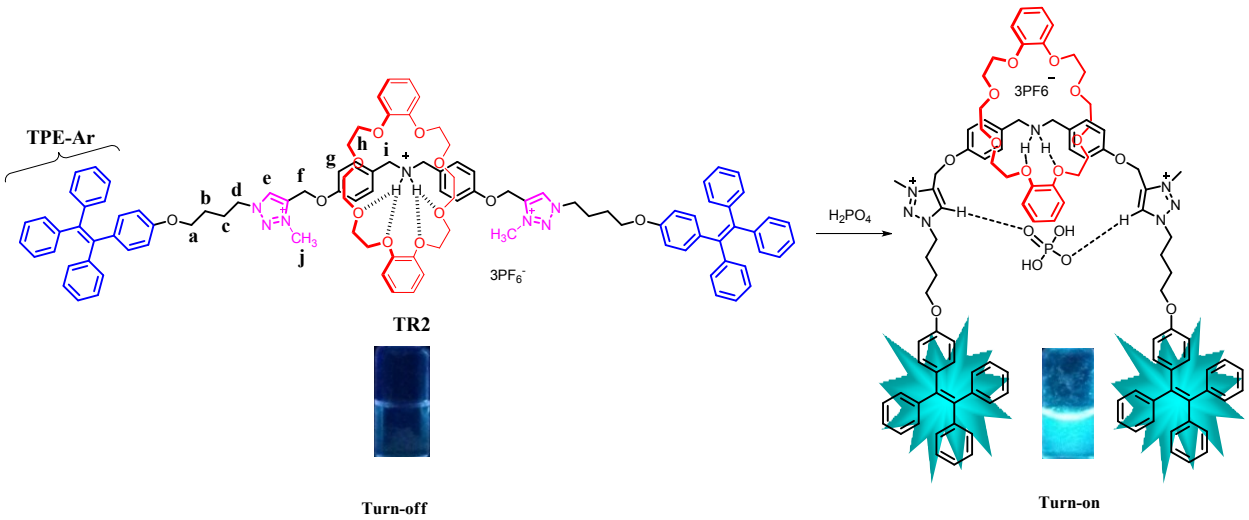


Fig. S18 A possible proposed binding mechanisms for [2]rotaxane **TR2** towards $H_2PO_4^-$ ion.

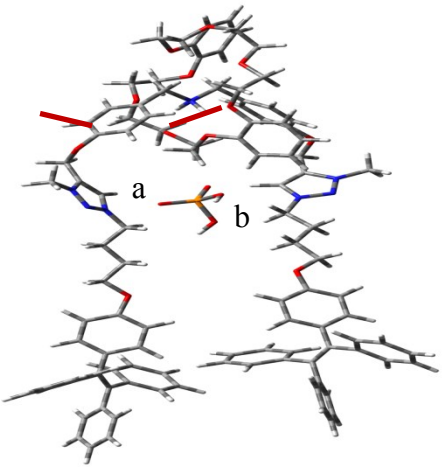


Fig. S19 Optimized chemical structures of complexes [2]rotaxane **TR2**-$H_2PO_4^-$ at the PM6 level. [Selected H-bond lengths (a) C-H…O: 1.978 Å; (b) C-H…O: 1.850 Å

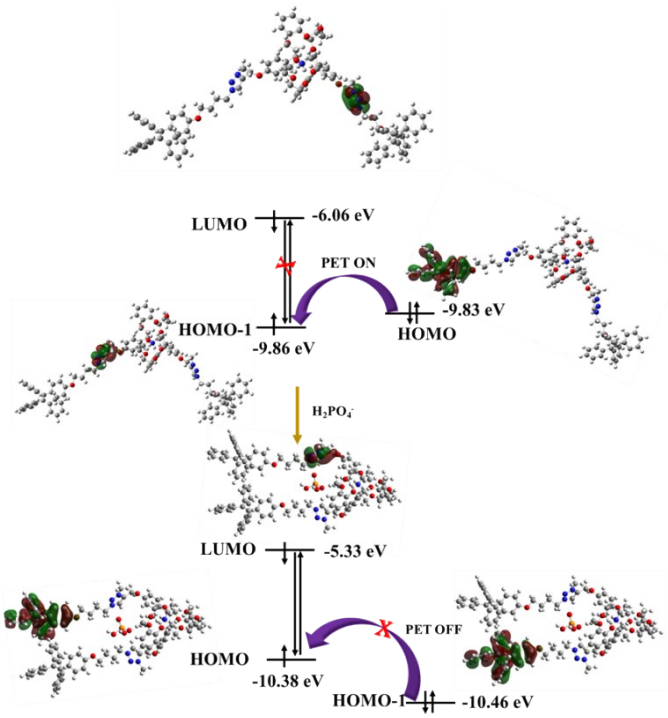


Fig. S20 Frontier molecular orbital diagram of [2]rotaxanes **TR2** and **TR2**-$H_2PO_4^-$ in gas phase at PM6 level.

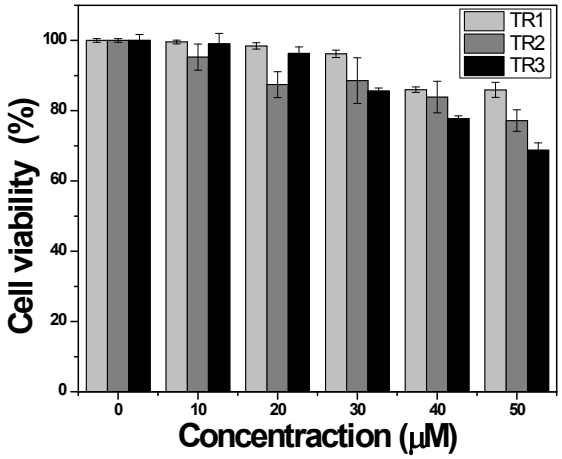


Fig. S21 Relative cell viability values (%) of Raw 264.7 cells estimated by an MTT assay versus incubated with **TR1, TR2** and **TR2** at different concentrations (0–50 μM) at 37 ˚C for 24 h.

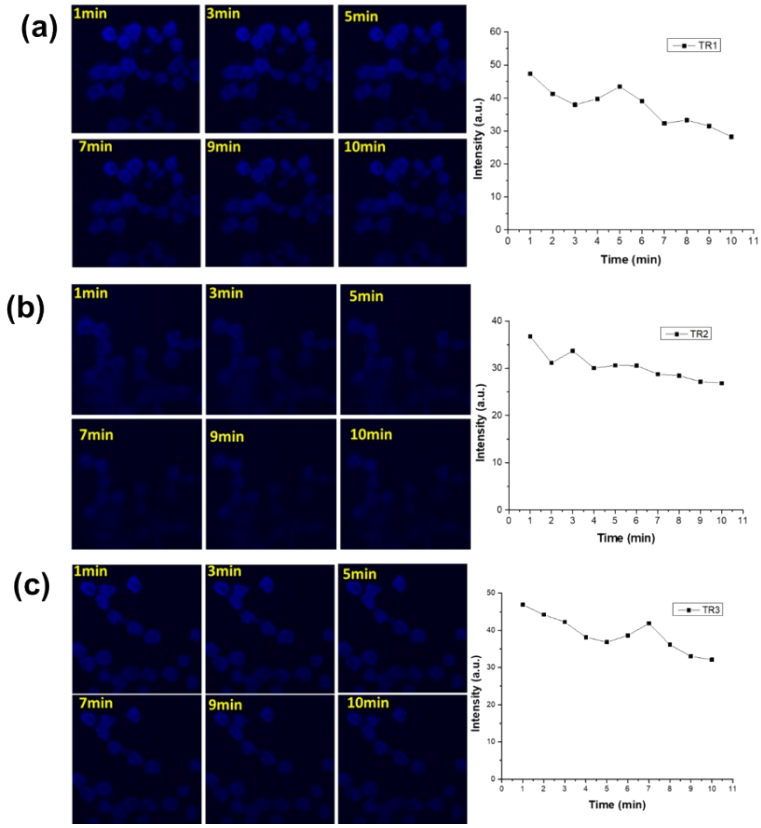


Fig. S22 Photostability tests of [2]rotaxanes (20 μM) (a) **TR1**, (b) **TR2** and (c) **TR3** in Raw 267.7 cells acquired at different scanning time. (λ_{ex} = 380 nm)

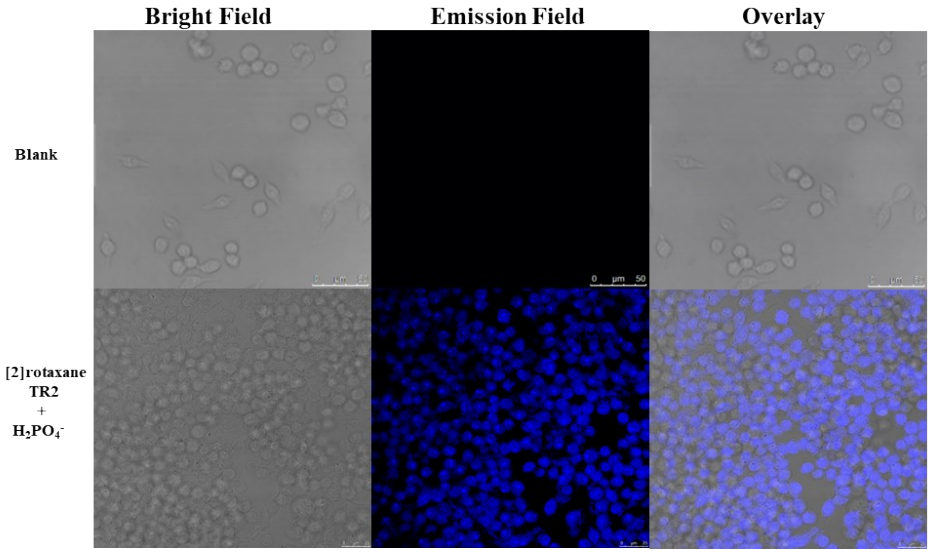


Fig. S23 Confocal microscopic images (with an excitation wavelength of λ_{ex} = 360 nm) of (top) RAW 264.7 cells incubated with [2]rotaxane **TR2** (10 μM) for 30 min and (bottom) further incubated with dihydrogen phosphate $H_2PO_4^-$ (20 μM) for 10 min; (left) bright- field transmission images, (center) emission-field images, and (right) overlay images.

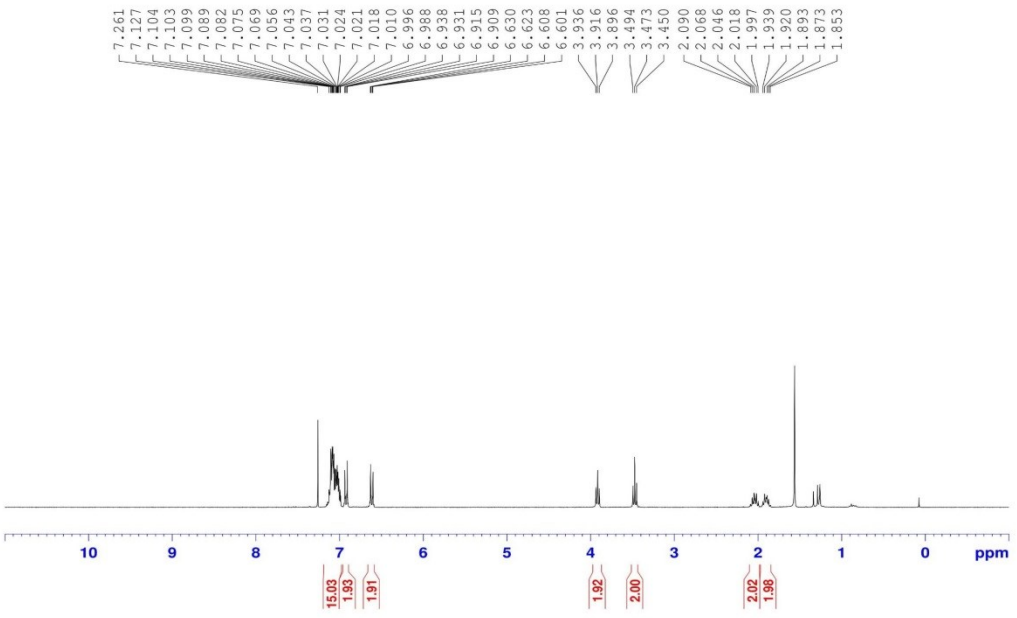


Fig. S24 ^{1}H **NMR** (300 MHz, CD_3Cl) spectrum of compound **S2**.

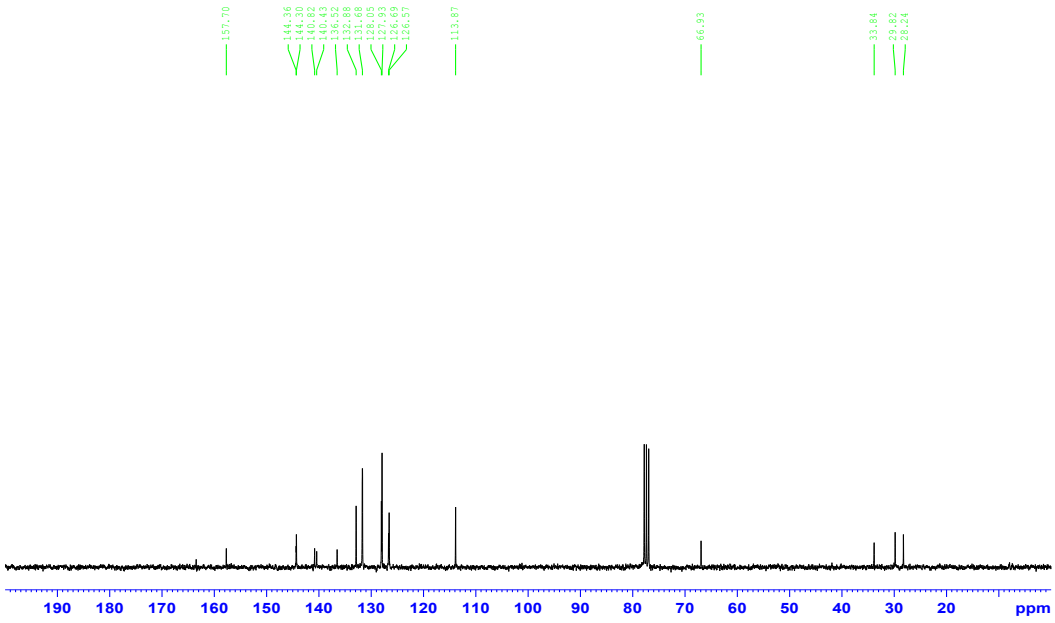


Fig. S25 ^{13}C **NMR** (75 MHz, CD_3Cl) spectrum of compound **S2**.

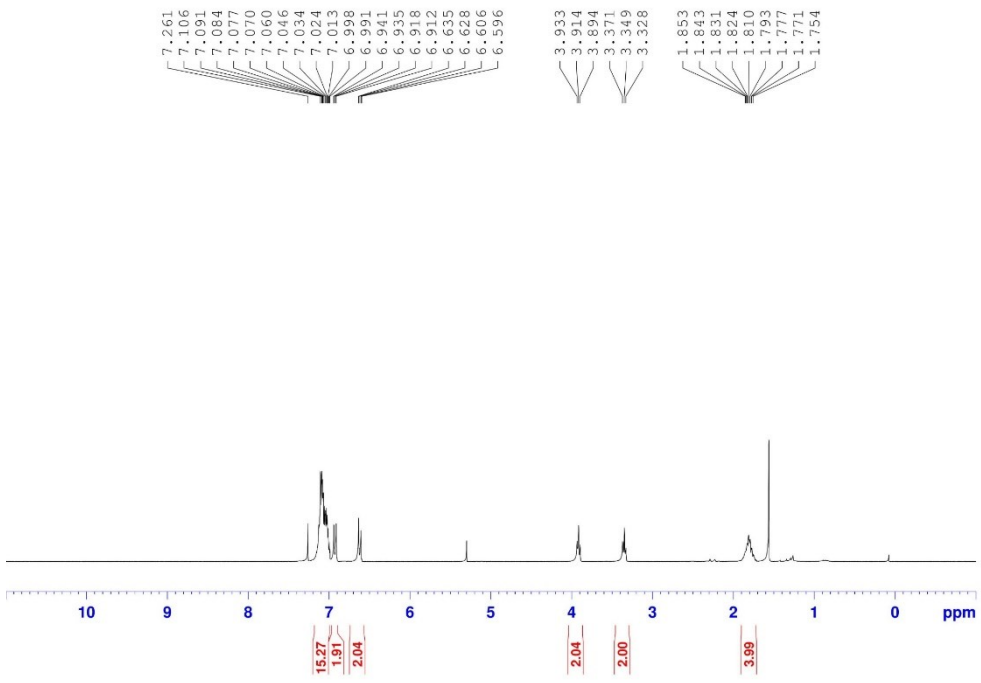


Fig. S26 ^{1}H **NMR** (300 MHz, CD_3Cl) spectrum of compound **S3**.

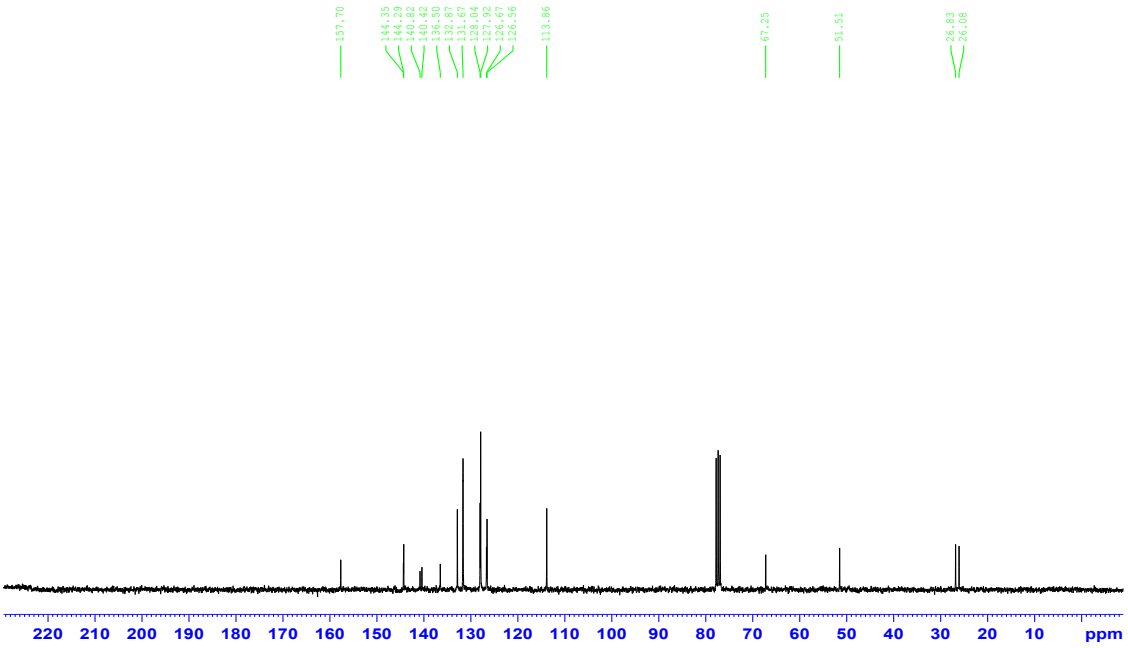


Fig. S27 ^{13}C **NMR** (75 MHz, CD_3Cl) spectrum of compound **S3**.

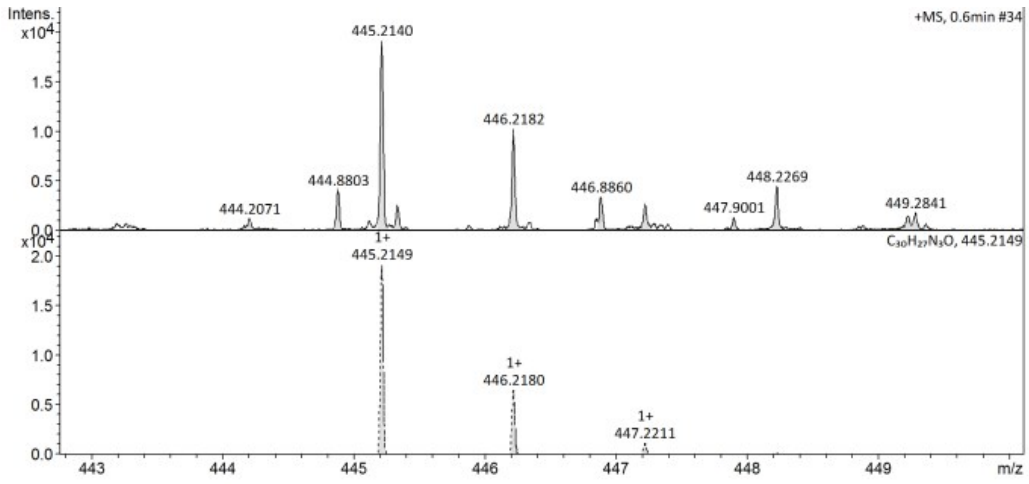


Fig. S28 HRMS ESI (+)-MS spectrum of compound **S3**.

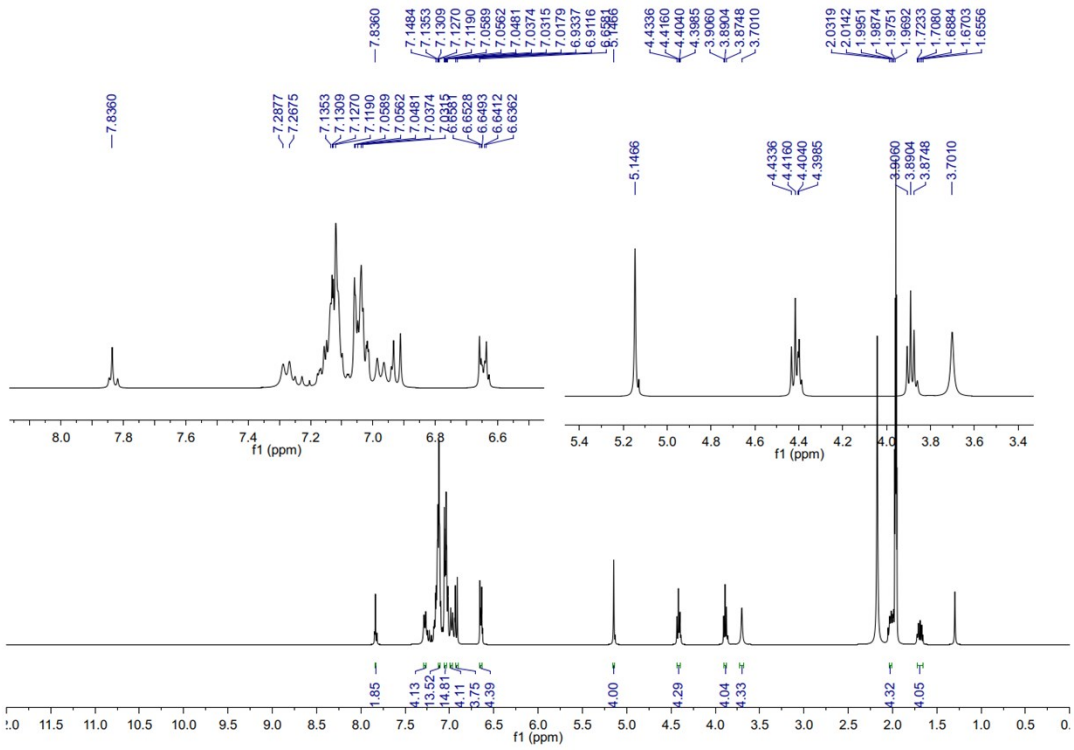


Fig. S29 ^{1}H **NMR** (400 MHz, CD_3CN) spectrum of compound **A1**.

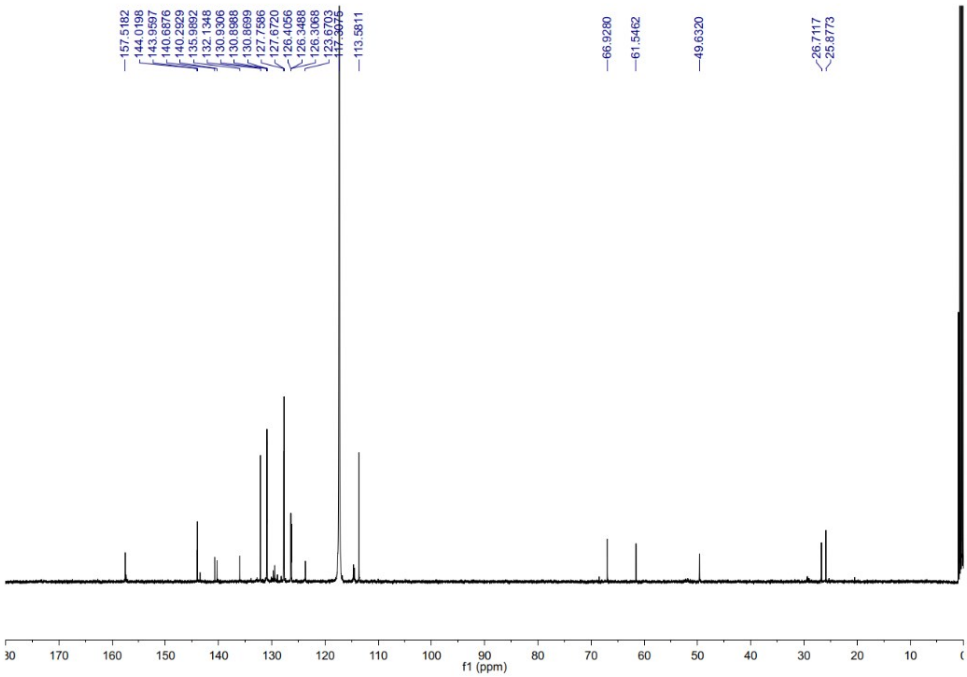


Fig. S30 ^{13}C **NMR** (100 MHz, CD_3CN) spectrum of thread **A1**.

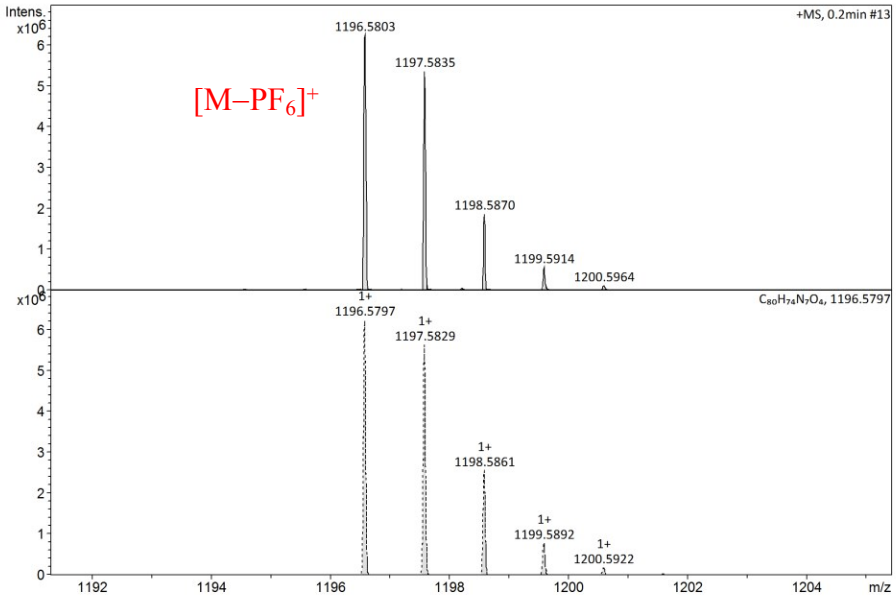


Fig. S31 HRMS ESI (+)-MS spectrum of thread **A1**.

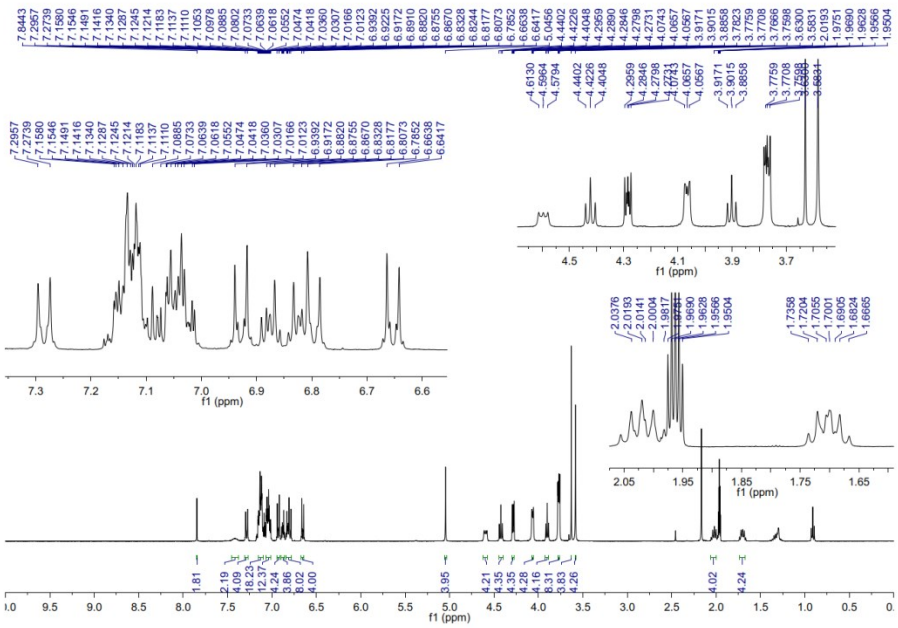


Fig. S32 ^{1}H **NMR** (400 MHz, CD_3CN) spectrum of compound **TR1**.

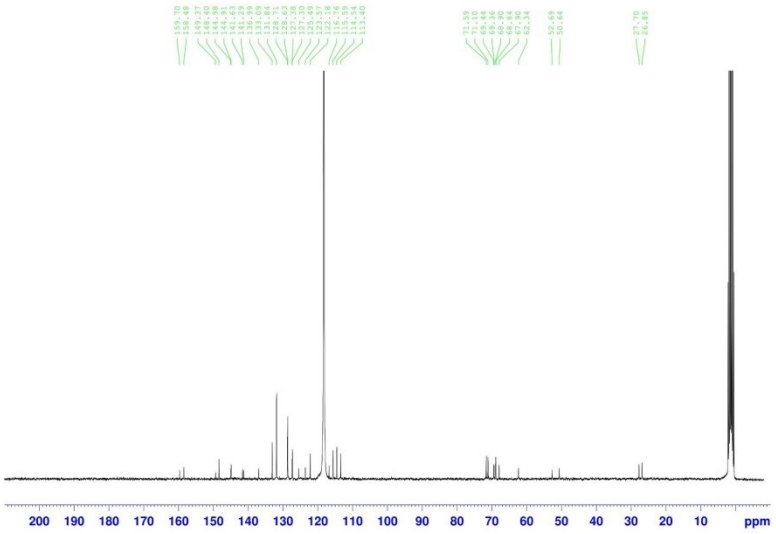


Fig. S33 ^{13}C **NMR** (75 MHz, CD_3CN) spectrum of compound **TR1**.

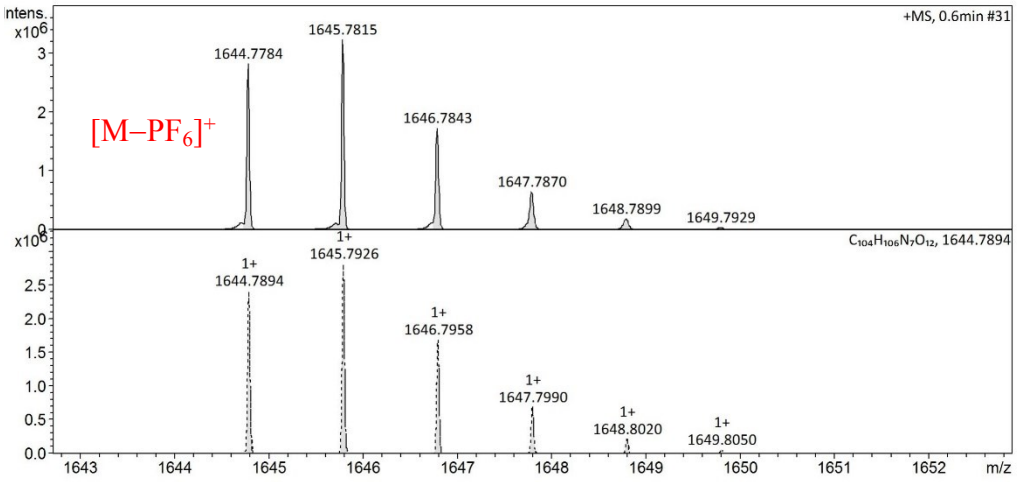


Fig. S34 HRMS ESI (+)-MS spectrum of compound **TR1**.

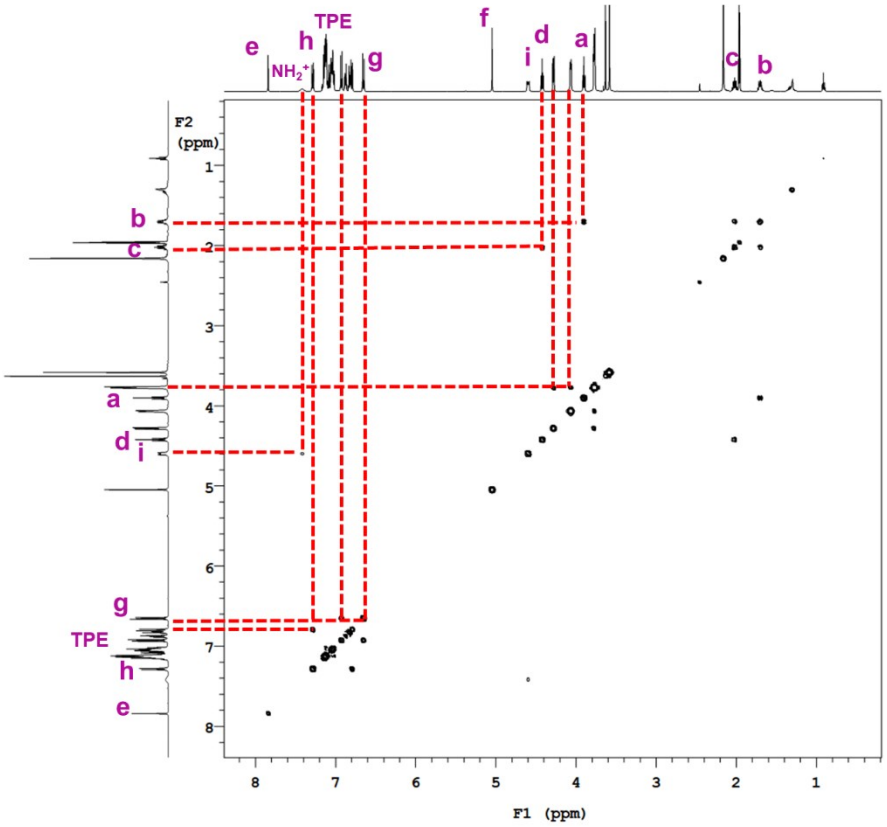


Fig. S35 ^{1}H-^{1}H COSY spectrum (500 MHz, 299.1 K, CD_3CN) of **TR1**.

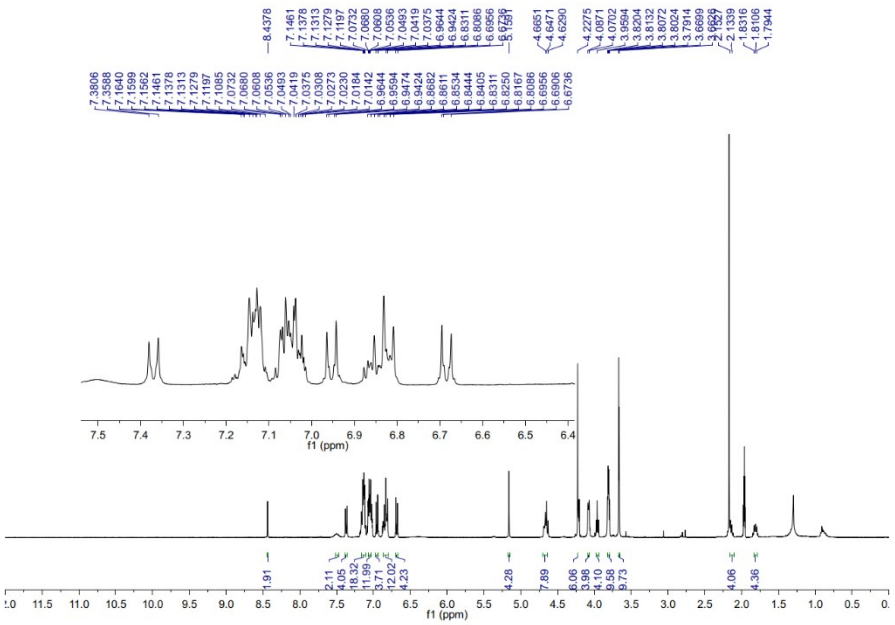


Fig. S36 ^{1}H **NMR** (400 MHz, CD_3CN) spectrum of compound **TR2**.

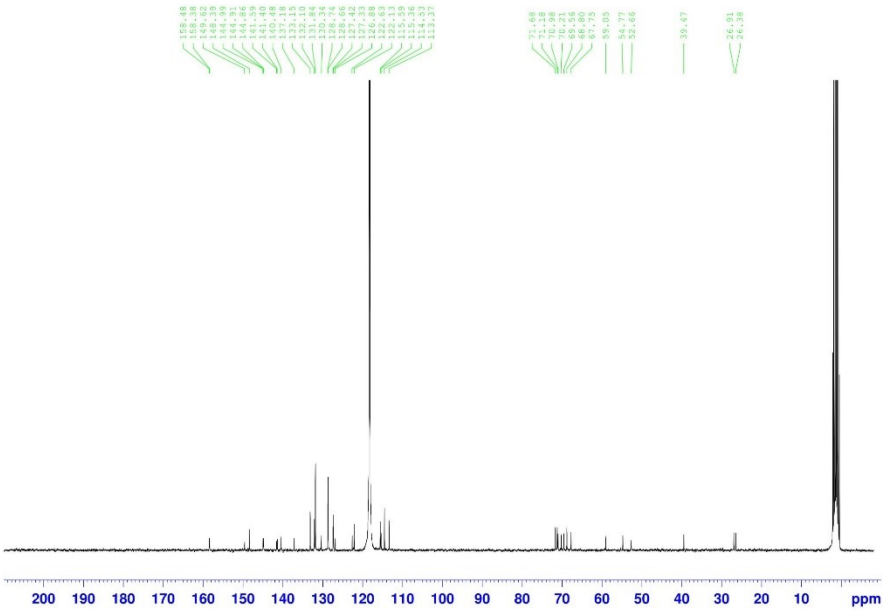


Fig. S37 ^{13}C **NMR** spectrum of compound **TR2**.

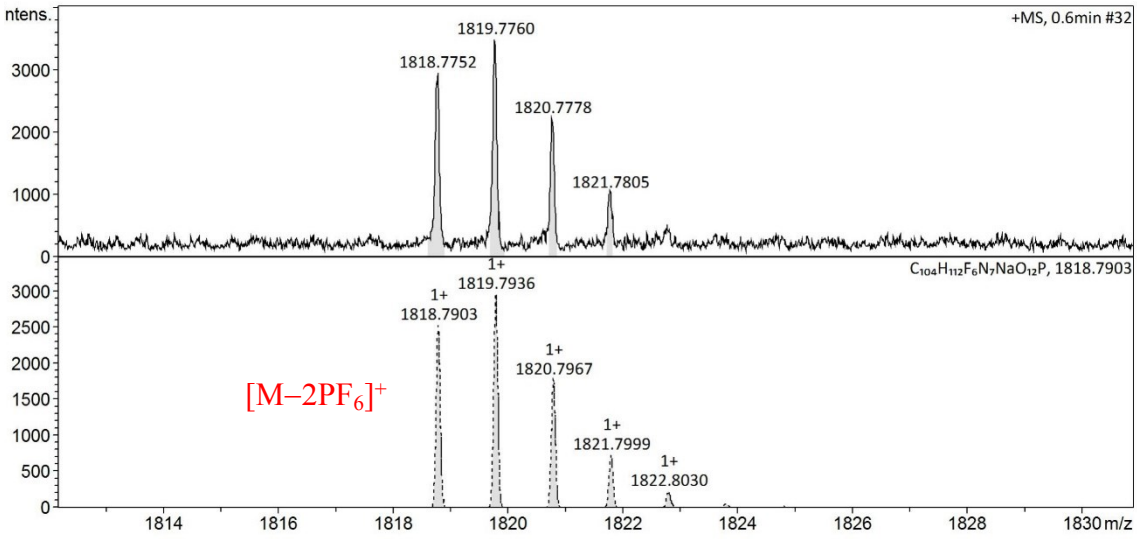


Fig. S38 HRMS ESI (+)-MS spectrum of compound **TR2**.

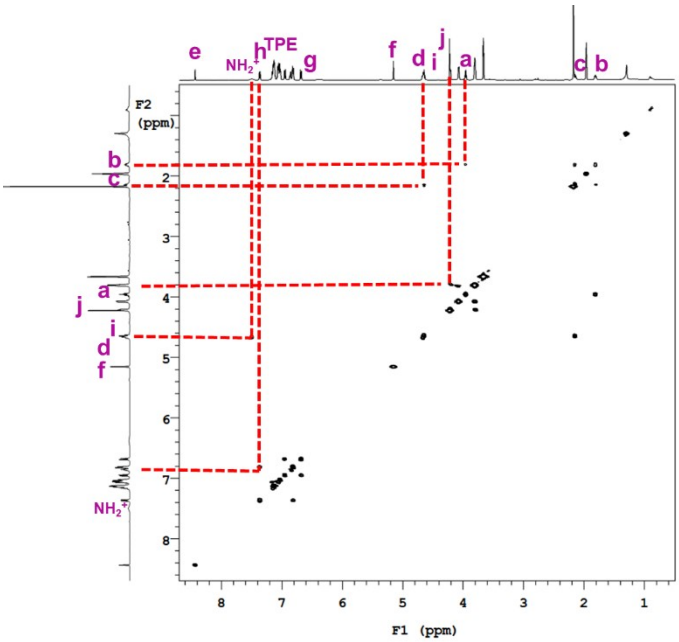


Fig. S39 ^{1}H-^{1}H COSY spectrum (500 MHz, 299.1 K, CD_3CN) of **TR2**.

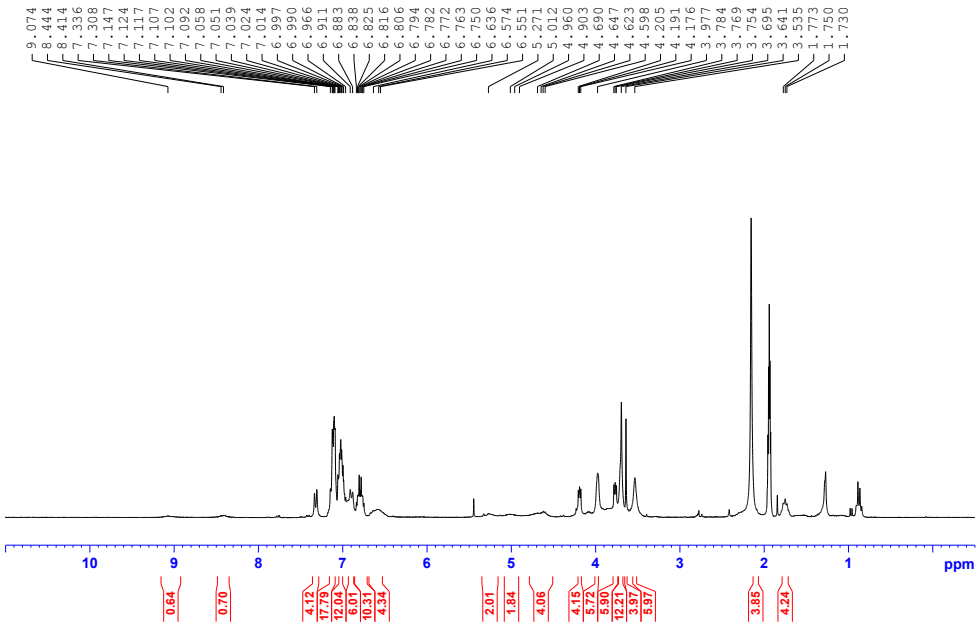


Fig. S40 ^{1}H **NMR** spectrum of compound **TR3**.

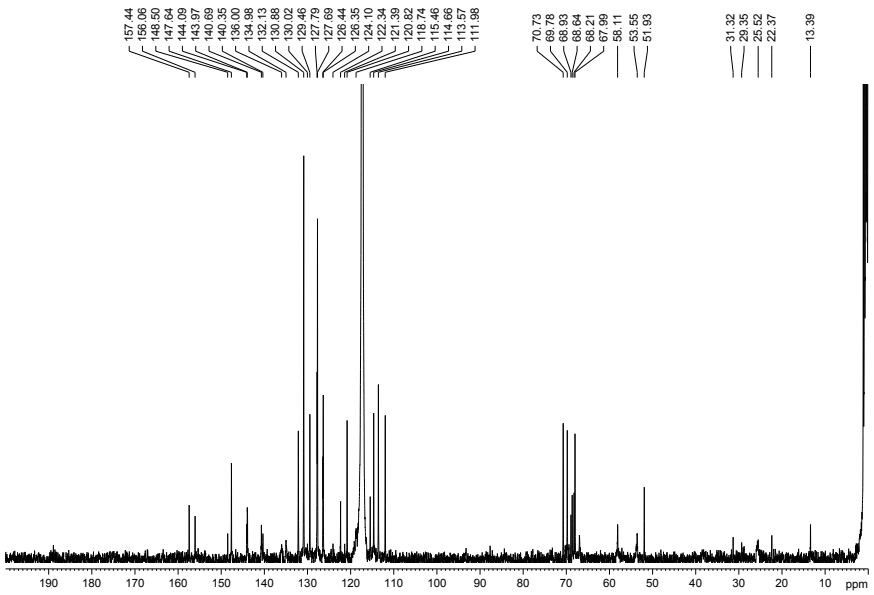


Fig. S42 ^{13}C **NMR** spectrum of compound **TR3**.

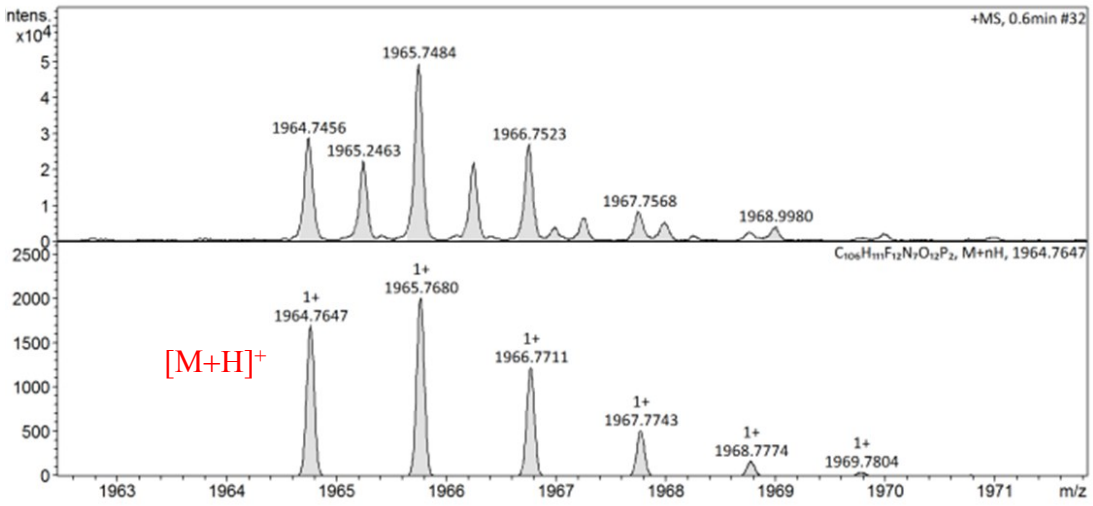


Fig. S42 HRMS ESI (+)-MS spectrum of compound **TR3**.

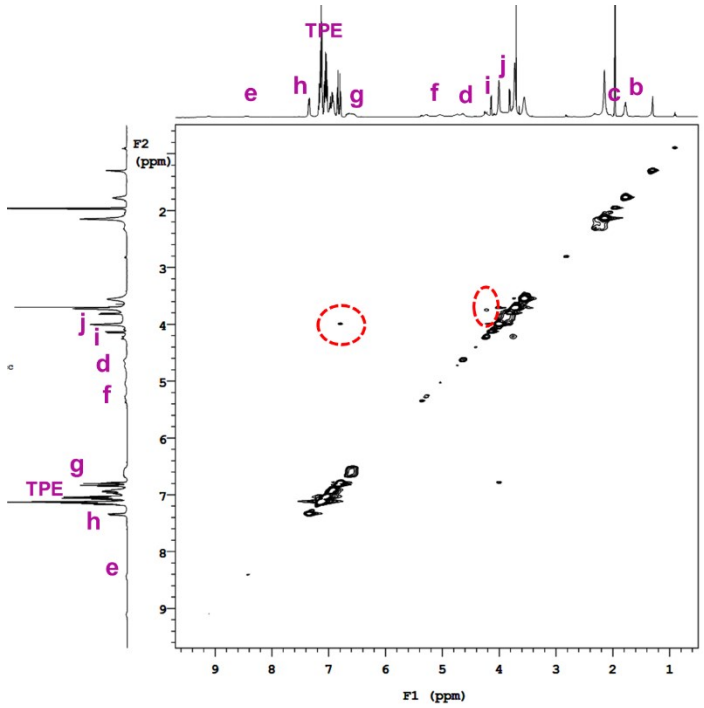


Fig. S43 ^{1}H-^{1}H ROESY spectrum (500 MHz, 300.1 K, CD_3CN) of **TR3**.

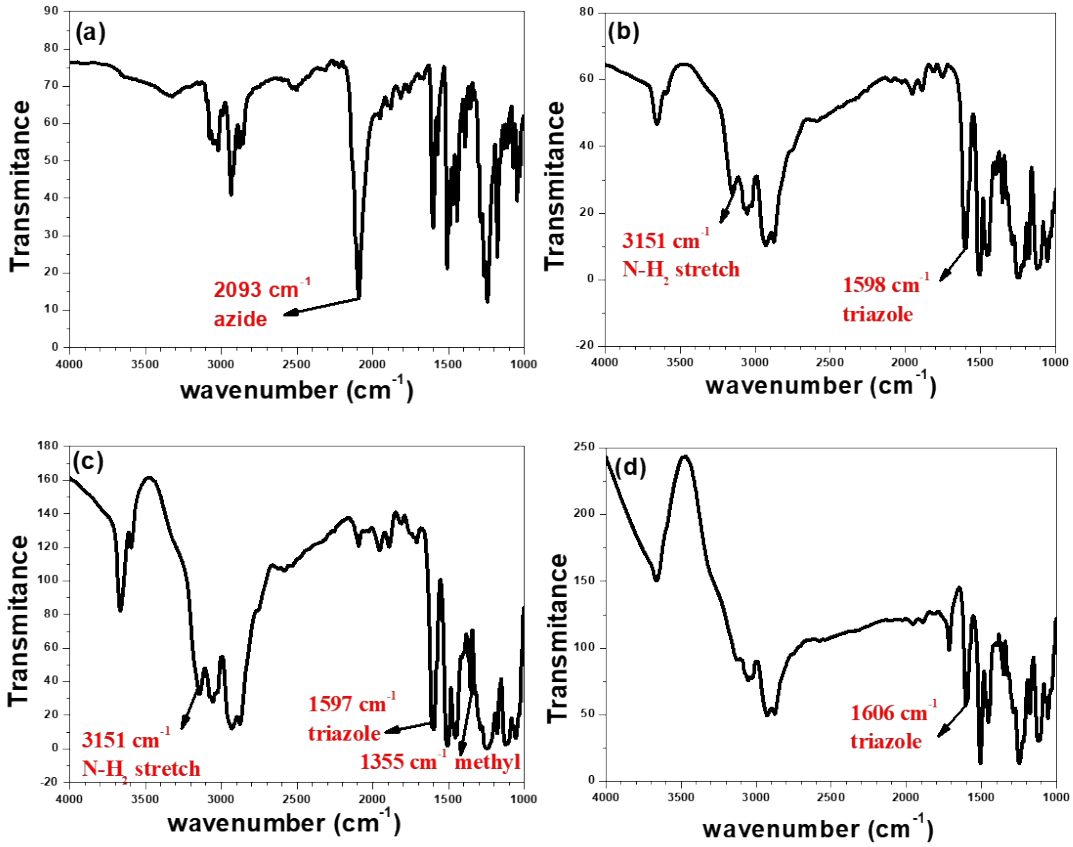


Fig. S44 FT-IR spectra of compounds (a) **S3**, (b) **TR1**, (c) **TR2** and (d) **TR3**.

References

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(S2) Z.-J. Zhang, H.-Y. Zhang, H. Wang, Y. Liu, A twin-axial hetero[7]rotaxane. *Angew. Chem. Int. Ed*., 2011, **50**, 10834−10838.