Electronic Supplementary Information

A Room Temperature Phosphorescence Encoding [2]Rotaxane Molecular Shuttle

Xiang Ma,* Jing Zhang, Jingjing Cao, Xuyang Yao, Tiantian Cao, Yifan Gong, Chunchang Zhao and He Tian

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai, 200237, P. R. China.

General

Solvents were either employed as purchased or dried prior to use by usual laboratory methods. Dichloromethane, acetonitrile and dimethylformamide were distilled over CaH_2. Triethylamine and pyridine were distilled from KOH. Thin-layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60/$F_{254.}$ The plates were inspected by UV light, and if required, developed in I_2 vapor. Column chromatography was performed on silica gel 60 (300-400 mesh). Melting points were determined on a Reichert Thermovar apparatus and reported uncorrected.

Starting materials

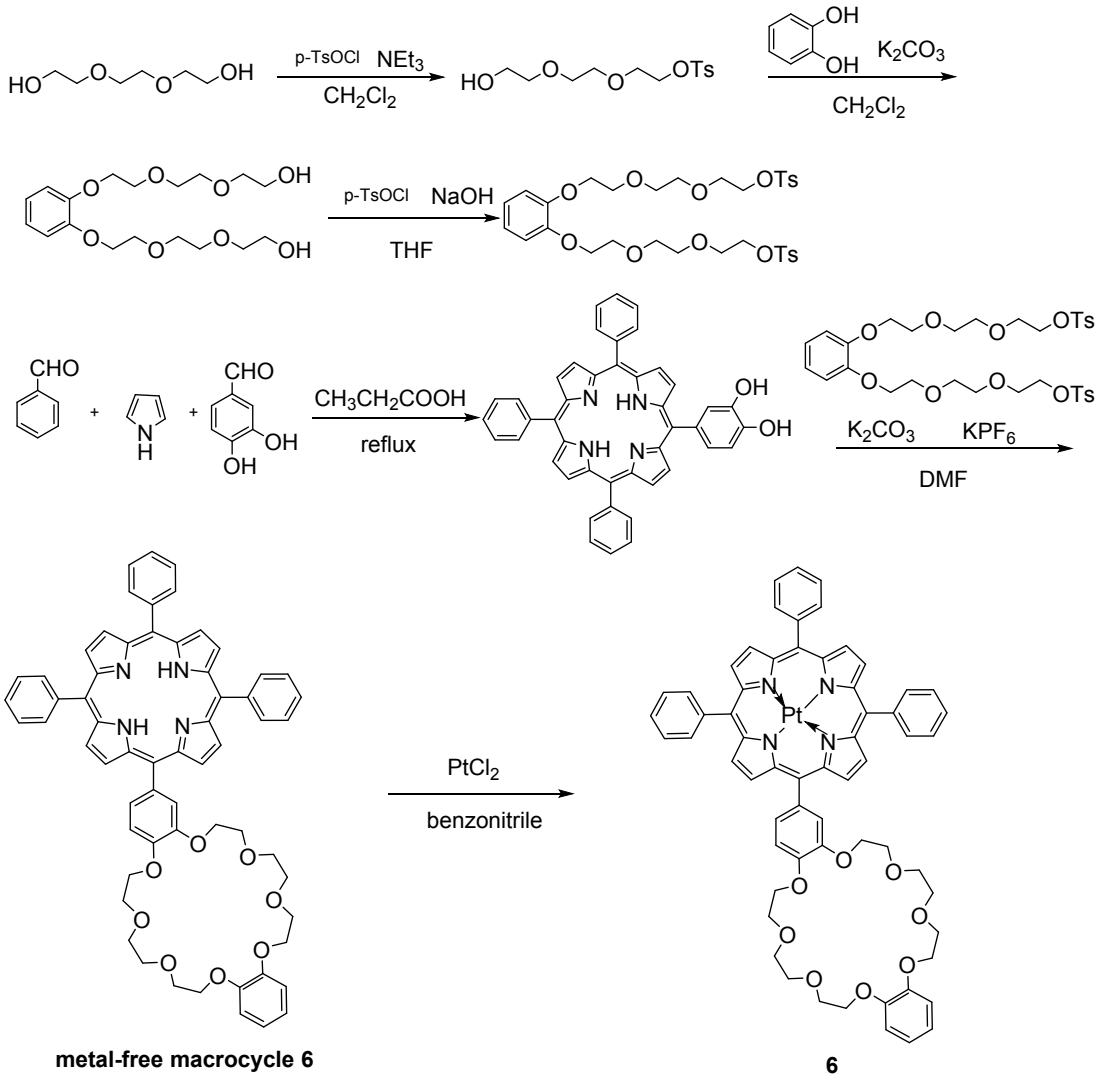
All chemicals were commercially available and used without further purification (unless mentioned). $NaBH_4$, NaH, NaN_3, $Cu(MeCN)_4PF_6$, K_2CO_3, KPF_6, NH_4PF_6, SDS, Na_2SO_3, aminoalcohol, di-tert-butyl dicarbonate, 1,4-dibromobutane, 4,4'-bipyridine, *p*-toluenesulfonyl chloride, catechol, triethylene glycol monotosylate, pyrrole, benzaldehyde, 3,4-dihydroxy benzaldehyde, propionic acid and dibenzo-24-crown-8 (DB24C8) were commercial available. 9-Anthraldehyde (*Synthesis*, 1995, 1115), 3,5-di-tert-butylbenzyl bromide (*Tetrahedron*, 2002, **58**, 2405), *p*-toluenesulfonic acid but-3-ynyl ester (*Org. Lett.* 2006, **8**, 713) were prepared according to literature procedures. Water used in all experiments was distilled twice.

Spectral Measurements (Instrumentation)

^{1}H-NMR spectra were measured on a Brüker AM 500 or 400 spectrometer at 25 °C. All chemical shifts are reported in ppm with residual solvents as the internal standards, and the coupling constants (*J*) are in Hertz. The following abbreviations were used for signal multiplicities: s, singlet; br, broad; d, doublet; t, triplet; m, multiplet. Mass spectra were recorded on a Brüker Biflex IV spectrometer. UV-Vis spectra were obtained on a Varian Cary 500 spectrophotometer at 25 °C (1 cm quartz cell used). Fluorescent spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer with 1 cm path cell. RTP spectra were carried out on a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a phosphorescence attachment at room temperature. A 150 W Xenon-pulsed lamp was used as the excitation light source and Obey-Decay application program was used for phosphorescence lifetime measurements. The instrument's main parameters are as follows: delay time 0.1 ms, gate time 2.0 ms, total decay time

20 ms, flash count 1, ex slit 10 nm, em slit 10 nm, scan speed 600 nm/min. Cyclic Voltammetry curves were carried out with a Versastate II equipment.

Typically, platinum porphyrin complex in CH_3CN solution of 1 ml and SDS solution of 1 ml were transferred into a comparison tube of 5 ml respectively with final concentration 4×10^{-6} mol/L and 0.5 mol/L, respectively. Then, Na_2SO_3 was added as an oxygen scavenger (final concentration 8 mmol/ L). After approximately 10 min incubation, the solution was diluted with water to the final volume of 5 ml. Then 3 ml of the resultant working solution was immediately transferred into 1 cm quartz cell equipped with a cover and then RTP and RTP lifetime tests were taken. All the fluorescence emission and fluorescence lifetime tests were carried out in the CH_2Cl_2 solution mixing with a small amount of CH_3CN.



Scheme S1. Synthesis route of the macrocycle **6.**

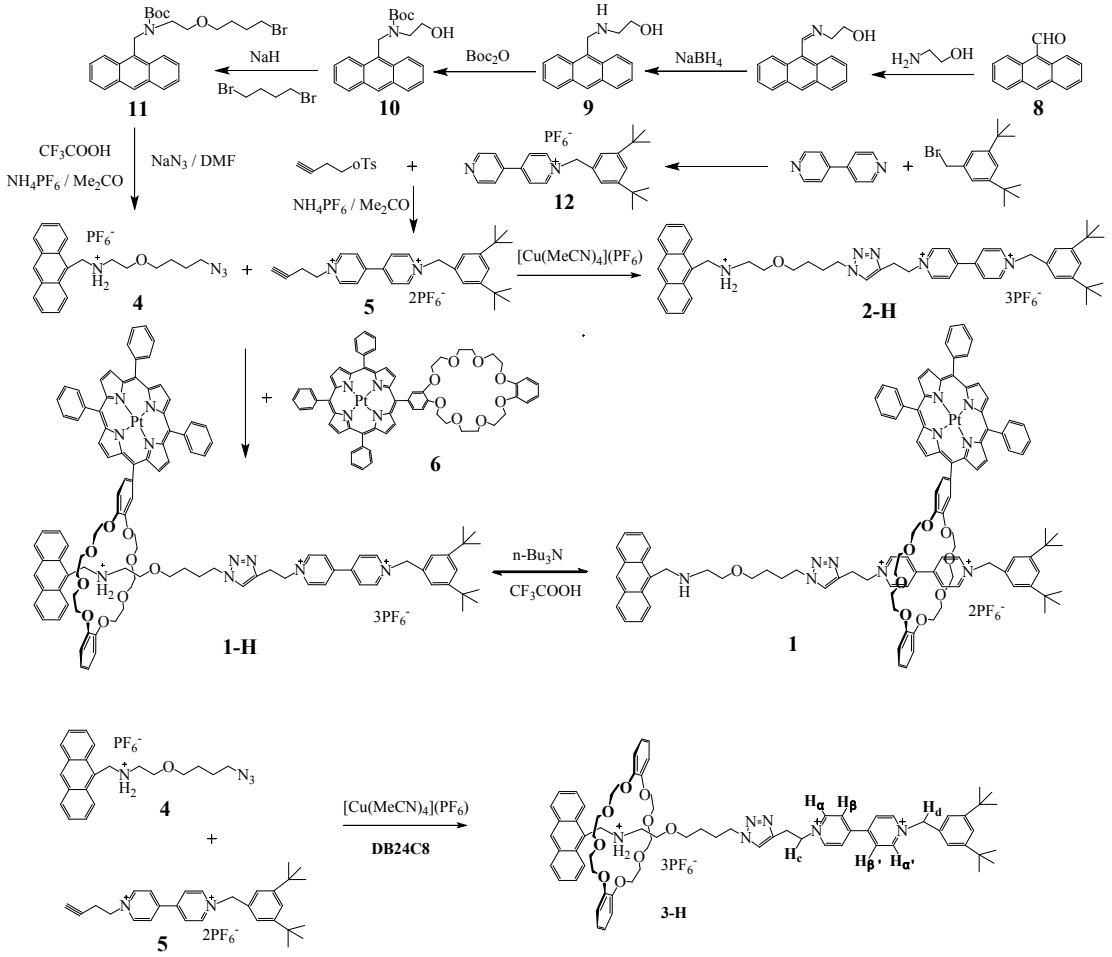
Synthesis of the macrocycle 6

The free-base porphyrin precursor (5-(3,4-dihydroxyphenyl)-10,15,20-triphenylporphyrin) was prepared following the Adler-Longo method[1]. In a 2L dry three-necked flask, the solution of benzaldehyde (20g, 189mmol) and 3,4-dihydrobenzaldehyde (8.7g, 63mmol) in propionic acid

(1000ml) was stirred and heated to 60 °C. The freshly distilled dry pyrrole (17ml) was added dropwise over 30min, then the mixture was heated to reflux slowly and further stirred for 1h. The mixture was cooled to room temperature and added into 1L 50% methanol (methanol : water = 1 : 1), then stayed in fridge for 24h. The purple precipitate was filtered, washed with 50% methanol, and the filter cake was dried in vacuum. The crude was chromatographed on silica gel to afford purple solid (0.35g，yield 8.6%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 8.82 (d, *J*=4.8 Hz, 8H), 8.21 (d, *J*=8.0 Hz, 6H), 7.77 (m, 11H), 7.29 (d, *J*=8.0 Hz, 1H), -2.79 (s, 2H). MS (ESI): m/z $[M+H]^+$ calc. for $C_{44}H_{31}N_4O_2^+$ 647.2, found 647.2.

The following 1,2-bis[2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy]benzene was synthesized according to classical procedures described in literature S2 in 3 steps with an overall yield of approximately 47%. And then, the metal-free marocycle was synthesized as follow: In a 100ml three-necked flask, the solution of sodium carbonate (430mg, 3.1mmol) and potassium hexafluorophosphate (570mg, 3.1mmol) in dry DMF (20ml) was stirred for 10 min under argon. 5-(3,4-dihydroxyphenyl)-10,15,20-triphenylporphyrin (500mg, 0.77mmol) and 1,2-bis[2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy]benzene (528mg, 0.77mmol) were dissolved in dry DMF (20ml), and the mixture was added dropwise over 30 min. The system was heated to reflux and further stirred for 72h, then cooled to room temperature. The mixture was filtered, washed with water, and the filter cake was dried in vacuum. The crude was chromatographed on silica gel to afford purple crystal (0.37g，yield 49%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 8.88 (d, *J* = 4.8Hz, 2H), 8.83 (d, *J* = 4.8Hz, 6H), 8.21 (d, *J* = 6.4Hz, 6H), 7.82-7.70 (m,11H), 7.22 (d, *J* = 8.4Hz, 1H), 6.94-6.87 (m, 4H), 4.45 (t, *J* = 4.0Hz, 2H), 4.28 (t, *J* = 4.0Hz, 2H), 4.22 (t, *J* = 4.0Hz, 2H), 4.19 (t, *J* = 4.0Hz, 2H), 4.12 (t, *J* = 4.0Hz, 2H), 4.04-3.98 (m, 4H), 3.98-3.92 (m, 4H), 3.92-3.85 (m, 4H), -2.78 (s, 2H). MS (ESI): m/z $[M+H]^+$ calc. for 985.4, found 985.4.

At last, the macrocycle **6** was synthesized as follow: A mixture of benzonitrile (30ml) and platinum dichloride (160mg, 0.6mmol) was refluxed for 4h under argon. After cooling to room temperature, the metal-free macrocycle compound (150mg, 0.15mmol) was added and continued to reflux for 2h under argon atmosphere. The bulk solvent was evaporated under reduced pressure and the residue was poured into petroleum ether (100ml). The precipitate was collected by filtration and the solid was dissolved in dichloromethane (50ml). Then the precipitate was removed by filtration. The dichloromethane was evaporated and the crude was purified by flash column chromatography on silica gel to afford an red solid (145mg, yield 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 3.5-4.6 (m, 24H), 7.1 (m, 4H), 7.8 (m, 11H), 8.2(m, 6H), 8.6 (s,1H), 8.9 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 148.91, 148.64, 146.94, 141.35, 141.10, 140.85, 140.80, 134.30, 133.85, 130.76, 130.68, 127.81, 127.10, 126.80, 122.29, 121.43, 119.73, 114.02, 111.76, 71.45, 71.35, 71.26, 69.99, 69.94, 69.89, 69.51, 69.40, 69.33, 29.69. MS (ESI): *m/z* [**6**] calc. for $C_{62}H_{54}N_4O_8Pt$ 1177.4, Found:1177.4.



Scheme S1. Synthesis route of the [2]rotaxanes **1-H, 1** and **3-H.**

Synthesis of the macrocycle

The free-base porphyrin precursor was prepared following the Adler-Longo method,[1] by allowing benzaldehyde react with freshly distilled dry pyrrole in refluxing propionic acid (141 °C). In addition, some modifications were developed in the purification process, namely, washing with MeOH/H_2O solution several times to remove the remaining propionic acid and undesired polymeric tars, as well as repeated chromatography separation from the other porphyrin byproducts. 1,2-bis[2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy]benzene was synthesized according to classical procedures described in literature[2] in 3 steps with an overall yield of approximately 47%. The synthesis of the macrocycle was carried out by reacting 1,2-bis[2-[2-(2-tosyloxyethoxy)ethoxy]benzene with 5-(3,4-dihydroxyphenyl)-10,15,20-triphenylporphrin in highly diluted solutions to reduce linear polymerization, in the presence of KPF_6 acting as a gathering centre to promote cyclization, the macrocycle compound was obtained as a purple crystal. Metallation of the porphyrin site of the macrocyclic complex affords the corresponding macrocycle **6** by addition of $PtCl_2$ to a solution of the free-base porphyrin-containing complex.

6: ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 3.5-4.6 (m, 24H), 7.1 (m, 4H), 7.8 (m, 11H), 8.2(m, 6H), 8.6 (s,1H), 8.9 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 148.91, 148.64, 146.94, 141.35, 141.10, 140.85, 140.80, 134.30, 133.85, 130.76, 130.68, 127.81, 127.10, 126.80, 122.29,

121.43, 119.73, 114.02, 111.76, 71.45, 71.35, 71.26, 69.99, 69.94, 69.89, 69.51, 69.40, 69.33, 29.69. MS (ESI): *m/z* [**6**] calc. for $C_{62}H_{54}N_4O_8Pt$ 1177.4, Found:1177.4.

Synthesis of *N*-(Anthracen-9-ylmethyl)amino Alcohols (9)[3]

To a stirred solution of aminoalcohol (12 mmol) in dry MeOH (10 mL) was added a solution of 9-anthraldehyde (10 mmol) in dry MeOH (10 mL) under argon. The mixture was stirred at room temperature overnight until the imine formation was complete (monitored by TLC). The solvent was evaporated under vacuum to give the crude imine as a bright-green solid, which was used for reduction without further purification. $NaBH_4$ (30 mmol) was added in small portions to the solution of imine in dry MeOH (20 mL) at 0 °C. The mixture was stirred at room temperature overnight and then concentrated under vacuum. The residue was dissolved in CH_2Cl_2 (50 mL) and washed three times with aqueous Na_2CO_3 (pH 10, 50 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: methane/chloroform, 1/9, R_f = 0.48) to give the bright yellow solid **9** (m.p. 116-118 °C; yield 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.40 (s, 1H), 8.20 (d, 2H), 8.00 (d, 2H), 7.48 (m,4H), 4.68 (s, 2H), 3.64 (t, 2H), 3.00 (t, 2H), 2.1 (br s, 2H).

Synthesis of N-Boc-N-(Anthracen-9-ylmethyl)amino Alcohol (10)[3]

The solution of N-(anthracen-9-ylmethyl)amino alcohol **9** (5 mmol) in 20 mL of pyridine/methanol (1:5 v/v) was stirred at 0 °C for 10 min. A solution of di-tert-butyl dicarbonate (7.5 mmol) in methanol (5 mL) was added dropwise over 10 min. The temperature was allowed to rise to room temperature and the reaction mixture was stirred overnight. The mixture was evaporated to dryness under reduced pressure. The residue was dissolved in methylene chloride and washed with deionized water several times. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel to give the desired product **10** as a pale-yellow solid (mp 131-132 °C, yield 84%; R_f = 0.21 (acetone/hexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.43(s, 1H), 8.38 (br s, 2H), 8.01 (d, 2H), 7.43 (m, 4H), 5.50 (br s, 2H), 3.30 (t, 2H), 3.00 (br s, 2H), 1.52 (br s, 9H).

Synthesis of 11

To a suspension of NaH (60% dispersion in mineral oil) in 7 mL of dry DMF was added dropwise **10** (600 mg, 2.65 mmol) at 0 °C under argon. A solution of 1, 4-dibromobutane (2.30 g, 10.7 mmol) in 3 mL DMF was then added to the solution. The reaction mixture was further stirred at room temperature for 20 h. Water was carefully added to quench the excess NaH after cooling the mixture to 0 °C. The aqueous layer was separated and extracted with EtOAc (3×50 mL). The extracts were washed with H_2O, dried over anhydrous $MgSO_4$, filtered, and the filtrate was concentrated in vacuum. The residue was chromatographed on silica gel (eluent: CH_2Cl_2, R_f = 0.5) to give the bromide **11** (352 mg, 36%) as an yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.49 (d, 2H, ^3J=8.8 Hz), 8.45 (s, 1H), 8.02 (d, 2H, ^3J=8.3 Hz), 7.50 (m, 4H), 5.60 (s, 2H), 3.39 (t, 2H, ^3J=6.7 Hz), 3.24 (m, 4H), 2.99 (d, 2H), 1.88 (m,2H), 1.63 (m, 2H), 1.54 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$): δ_C (ppm) 155.73, 131.55, 129.26, 129.15, 128.32, 126.38, 125.12, 124.81, 124.59, 79.99, 70.14, 69.78, 44.18, 42.36, 32.05, 31.56, 30.32, 28.41. HRMS (ESI): *m*/*z* [**11**+**Na**]$^+$ calc. for $C_{26}H_{32}BrNO_3$ 508.1463, found 508.1468.

Synthesis of 4

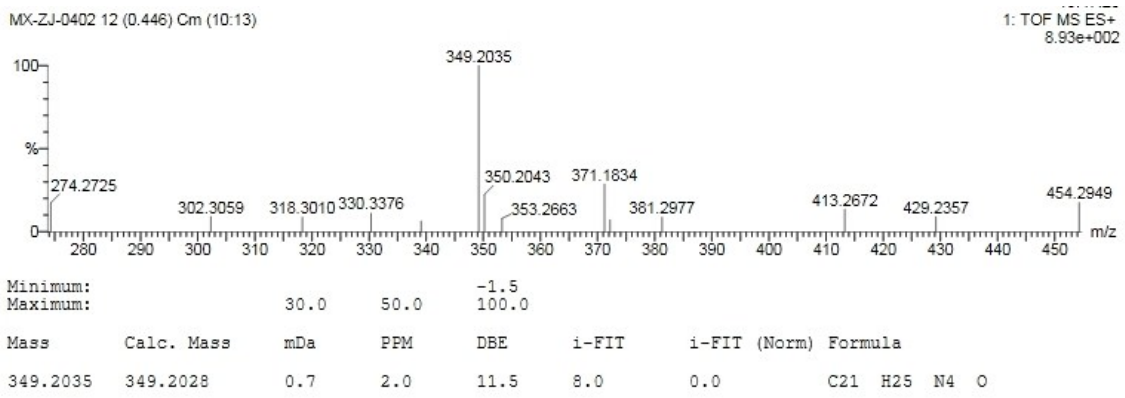
The bromide **11** (850 mg, 1.75 mmol) and NaN_3 (120 mg, 3.50 mmol) were dissolved in 10 mL DMF. The mixture was heated at 80°C for 24 h. Then the solvent was removed under reduced pressure, the residual was dissolved in CH_2Cl_2 (250 ml) and washed with water (350 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to obtain the azide compound as a yellowish solid (650 mg, 83%).^{1}H NMR (500 MHz, $CDCl_3$) δ_H (ppm) 8.50 (d, 2H, ^3J=4.1 Hz), 8.45 (s, 1H), 8.03 (s, 2H), 7.50 (m,4H), 5.60 (s, 2H), 3.29 (t, 2H, ^3J=6.0 Hz), 3.24 (m, 4H), 3.00 (d, 2H), 1.68 (m,2H), 1.60 (m, 2H),1.56 (s,9H). The azide compound was dissolved in CH_2Cl_2 (5 mL), before being treated with CF_3COOH (0.5 mL) after 3 h at room temperature, the solution was concentrated and the residue dissolved in CH_2Cl_2, the organic extracts were washed with saturated aqueous NH_4PF_6 solution, dried over anhydrous $MgSO_4$ and purified by chromatography on silica gel (yield 70%; R_f =0.48 (EtOAc)). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.40 (s, 1H), 8.33 (d, 2H, ^3J=8.8 Hz), 8.00 (d, 2H, ^3J=8.3 Hz), 7.56-7.45(m, 4H), 4.76 (s, 2H), 3.58 (t, 2H, ^3J=5.1 Hz), 3.40 (m, 2H), 3.21 (m, 2H), 3.03 (t, 2H, ^3J=5.3 Hz), 1.58 (m, 4H). ^{13}C NMR (100MHz, $CDCl_3$) δ_C (ppm) 134.28, 131.32, 131.02, 130.50, 129.81, 128.31, 127.34, 125.67, 122.44, 121.81, 70.70 65.53, 51.21, 47.40, 44.11, 26.52, 25.44. HRMS (ESI): *m*/*z* [**4-PF$_6$**]$^+$ calc. for $[C_{21}H_{25}NO]^+$ 349.2028, found 349.2035.

Synthesis of 3,5-Di-*tert*-butylbenzyl-4,4'-pyridylpyridinium Hexafluorophosphate (12) [4]

3,5-di-*tert*-butylbenzyl bromide (0.5 g, 1.8 mmol) in $CHCl_3$ (50 mL) was added dropwise to a refluxing solution of 4,4'-bipyridine (1.11 g, 7.1 mmol) in $CHCl_3$ (50 mL) over 2 h, then the solution was stirred and heated under reflux for 3d. After evaporation of the solvent in vacuo, the residual solid was suspended in Me_2CO (30 mL), before being treated with an aqueous solution of NH_4PF_6 (0.86 g, 5.3 mmol) in order to achieve complete dissolution. The Me_2CO was evaporated off, then the precipitate formed was collected, washed thoroughly with ethyl ether and air-dried to give **12** (0.67g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 9.44 (d, 2H), 8.86 (d, 2H), 8.67 (d, 2H), 7.96 (d, 2H), 7.61 (s, 3H), 6.10 (s, 2H), 1.32 (s, 18H).

Synthesis of 5 [5]

A solution of **12** (440 mg, 1 mmol) and p-toluenesulfonic acid but-3-ynyl ester (400mg, 1.8mmol) in MeCN (10 ml) was heated to 80 °C under Ar for 4 d. The solution was then cooled to room temperature and the resulting precipitate was filtered and washed with MeCN. The yellowish solid was then dissolved in a H_2O/Me_2CO (3:1) mixture and a saturated aqueous solution of NH_4PF_6 was added to this mixture. The resulting precipitate was filtered, washed with H_2O, and air-dried to give **5** (661 mg, 95%). ^{1}H NMR (400MHz, DMSO-d_6): δ_H (ppm) 9.59 (d, ^3J = 6.8Hz, 2H), 9.39 (d, ^{3}J = 6.8Hz, 2H), 8.79 (t, ^{3}J = 6.9, 4H), 7.55 (d, ^{3}J = 1.4Hz, 2H), 7.47 (s, 1H), 5.87 (s, 2H), 4.84 (t, ^{3}J = 6.5Hz, 2H), 3.11 (t, ^{3}J = 2.4Hz, 1H), 3.07-2.99 (m, 2H), 1.30 (s, 18H). ^{13}C NMR (100MHz, DMSO-d_6): δ_C (ppm) 151.59, 149.20, 148.88, 145.91, 145.40, 133.32, 127.20, 126.46, 123.31, 123.19, 78.99, 75.28, 64.21, 58.77, 34.70, 31.11, 20.31. HRMS (ESI): *m*/*z* [**5-PF$_6$**]$^+$ calc. for $[C_{29}H_{36}F_6N_2P]^+$ 557.2515, found 557.2507.



Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
349.2035	349.2028	0.7	2.0	11.5	8.0	0.0	C21 H25 N4 O

Fig. S1 ESI-MS spectrum of the azide **4.**

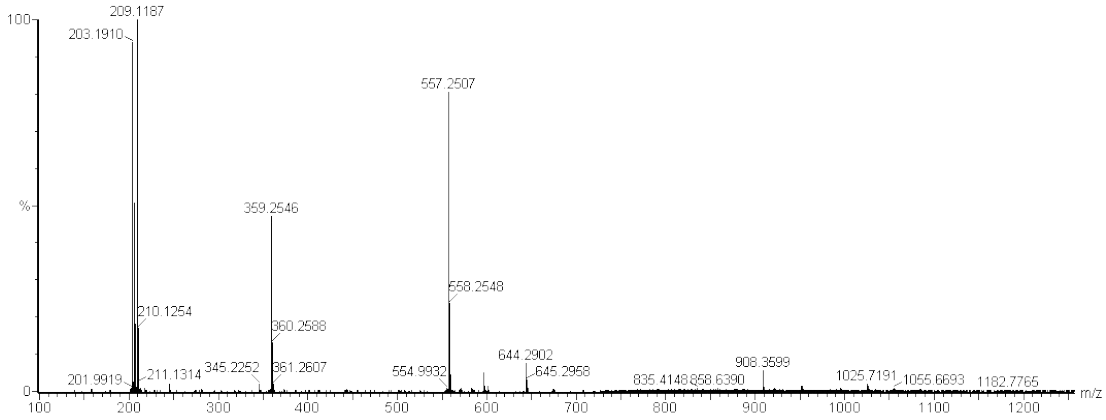


Fig. S2 ESI-MS spectrum of the $BIPY^{2+}$ derivative **5.**

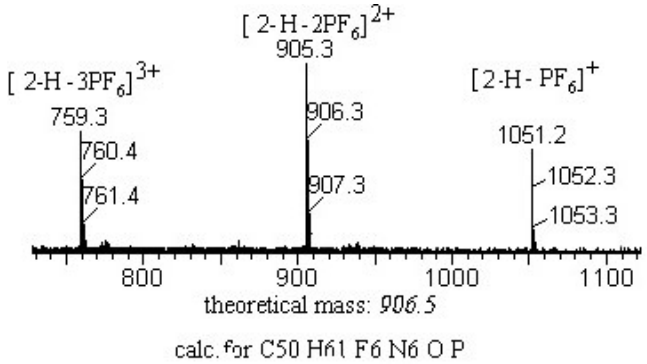


Fig. S3 ESI-MS spectrum of the thread **2-H.**

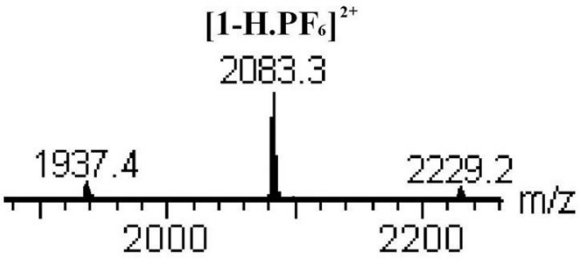


Fig. S4 ESI-MS spectrum of the [2]rotaxanes **1-H.**

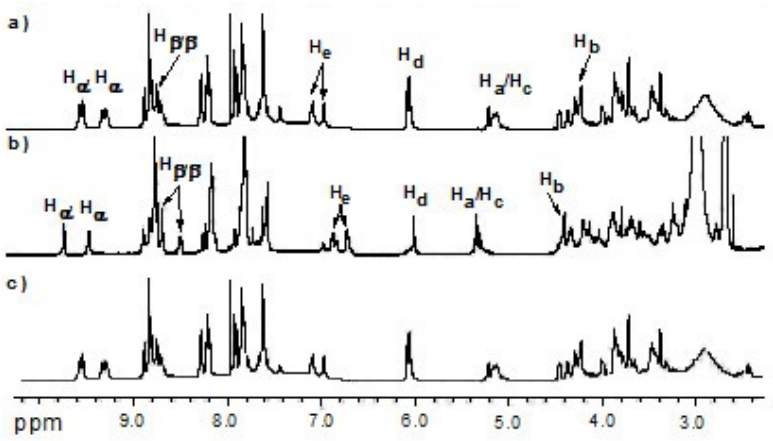


Fig. S5 Partial ^{1}H NMR spectra (500 MHz in CD_3COCD_3 at 298 K) of: (a) [2]rotaxane **1-H**; (b) the deprotonated [2]rotaxane **1** and (c) **1** after adding CF_3COOH.

Table S1. Absorption bands of **1-H/1, 2-H/2, 3-H/3, 6 and 7** (**298K**, CH_3CN, 10^{-5} M).

Compound	B $_{(0,0)}$ Soret band		Q $_{(0,0)}$	
	λ_{max} / nm	ϵ (L mol^{-1} cm^{-1})	λ_{max} / nm	ϵ (L mol^{-1} cm^{-1})
6	400	95200	508	8900
7	422	108100	556	5470
1-H/1	400	95300	508	6440
3-H/3	422	103500	556	7290

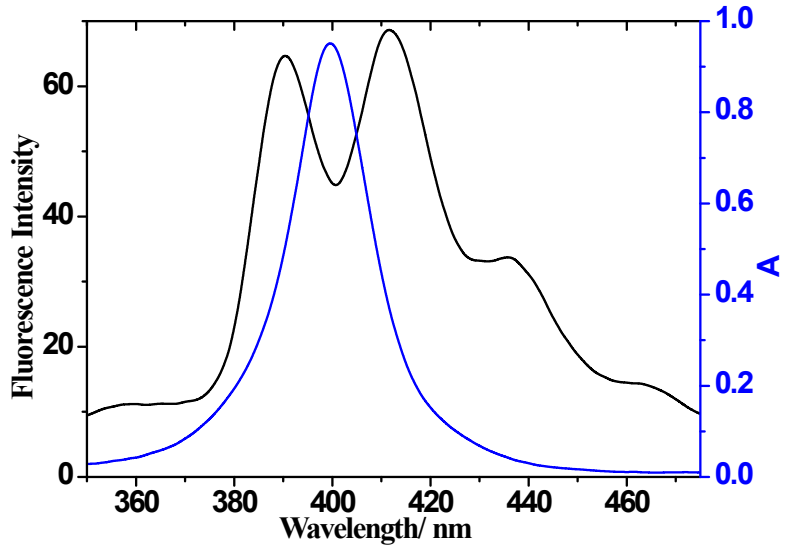


Fig. S6 Overlap of fluorescence emission spectra of the Anth moiety (black line, λ_{ex}= 370 nm) and absorption spectra of the porphyrin moiety (blue line) of **6**.

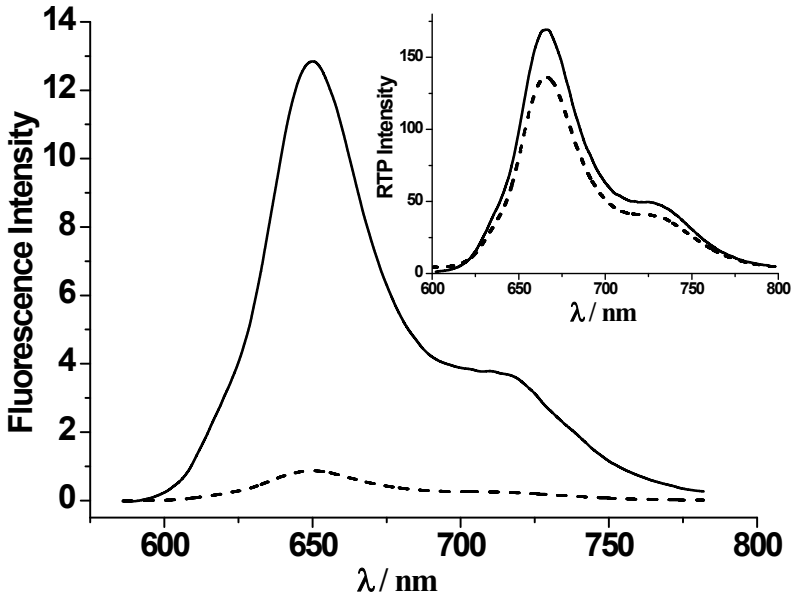


Fig. S7 Fluorescence emission spectra of **6** (solid line) and **1-H** (dashed line), 1.0×10^{-5} mol/L, λ_{ex}= 402 nm. Inset: **RTP** emission spectra of **1-H** (solid line) and **6** (dashed line), 4.0×10^{-6} mol/L, λ_{ex}= 402 nm.

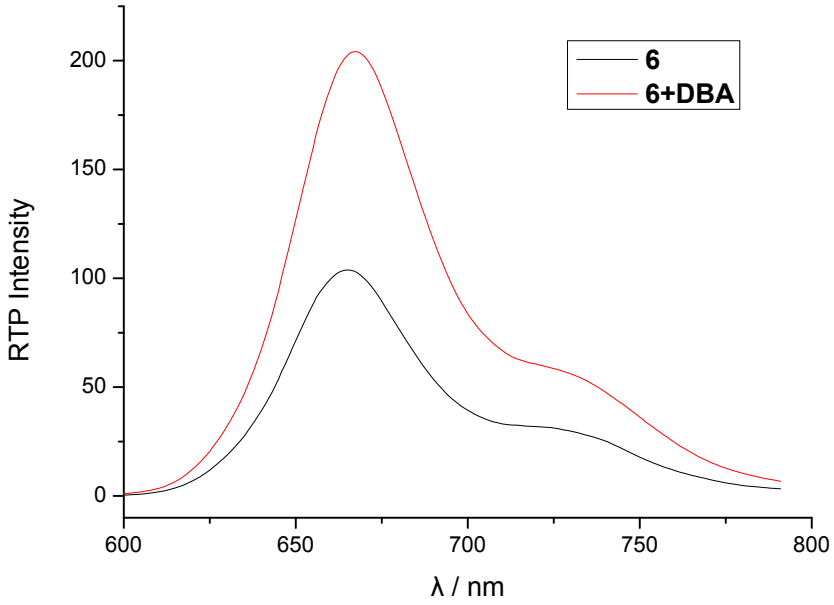


Fig. S8 RTP emission spectra of a mixture of **6** and after addition of dibenzylammonium hexafluorophosphate (**DBA**) (1:1) at 298K (4×10^{-6} mol/L, λ_{ex} = 402 nm).

We conducted a control experiment, in which the porphyrin-containing macrocycle **6** was threaded by a new guest molecule dibenzylammonium hexafluorophosphate (**DBA**). The RTP emission of this mixture (probably forming the pseudorotaxane-like complex with the ratio of 1:1 according to the previous reports, Fig. S8) showed an increase comparing with the single macrocycle **6** under the same test conditions. This increase effect of RTP emission should be due to the movement restriction of the macrocycle **6** in the pseudorotaxane system.

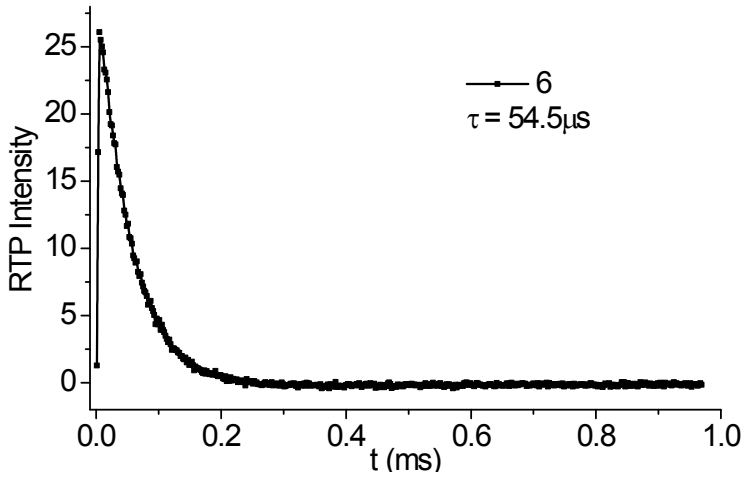


Fig. S9 RTP Lifetime of the ring **6** (λ_{ex} = 408 nm, monitored at 667 nm).

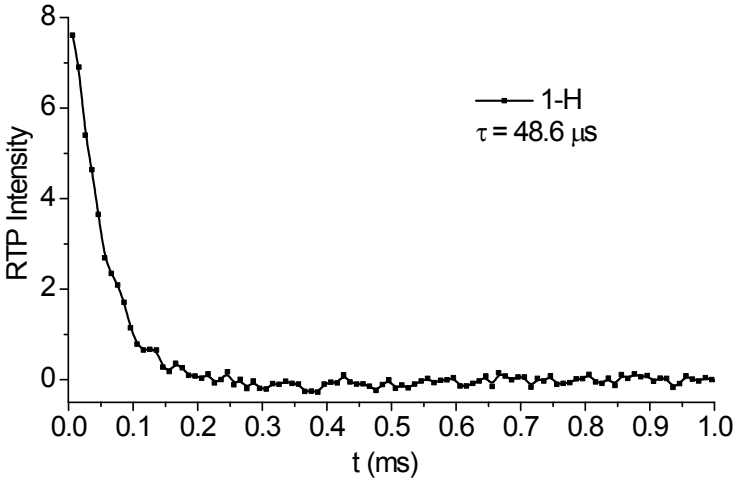


Fig. S10 RTP Lifetime of the [2]rotaxanes **1-H** (λ_{ex} = 403 nm, monitored at 665 nm).

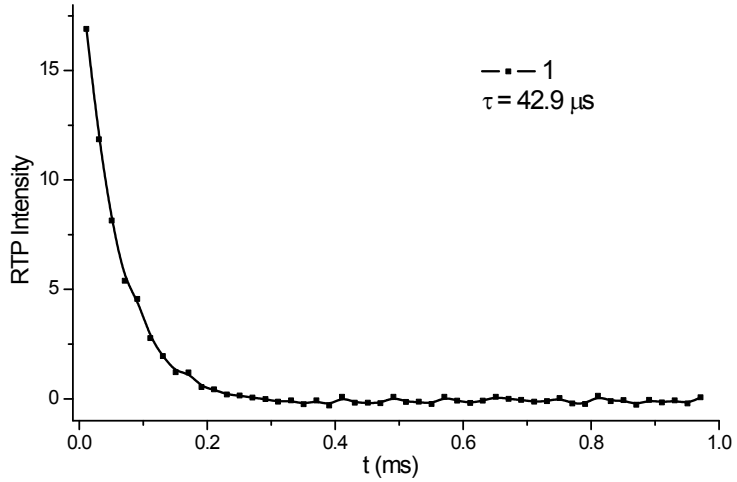


Fig. S11 RTP Lifetime of the [2]rotaxanes **1** (λ_{ex} = 403 nm, monitored at 666 nm).

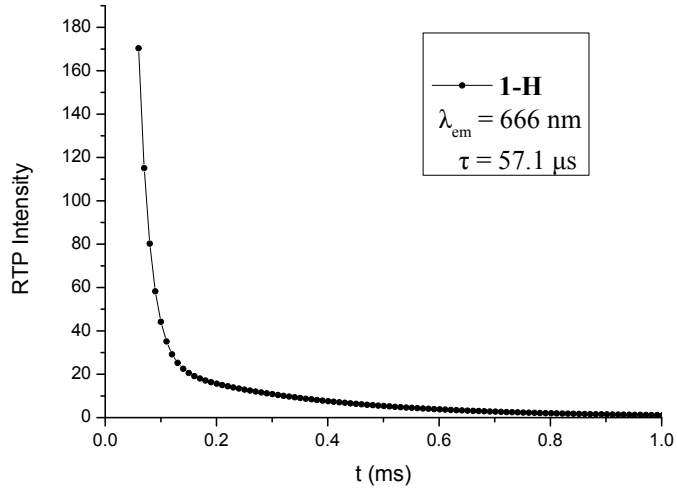


Fig. S12 RTP Lifetime of the [2]rotaxanes **1-H** (λ_{ex}= 370 nm， monitored at 666 nm, 4×10^{-6} mol/L).

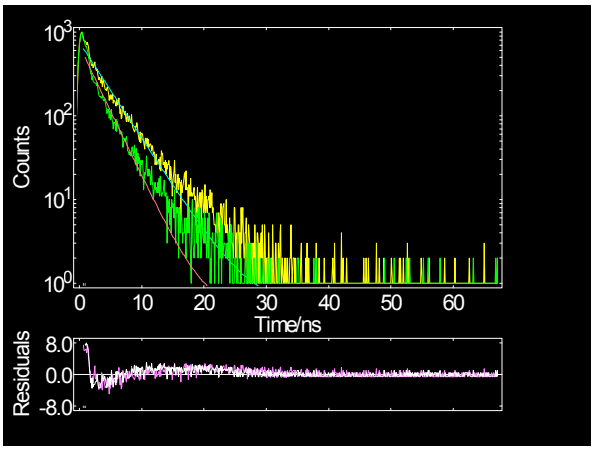


Fig. S13 Fluorescence Lifetime of the [2]rotaxanes **1-H/1**. The lifetimes were found 2.79 ns for **1-H** and 3.79 ns for **1** (λ_{ex} = 370 nm, monitored at 390 nm).

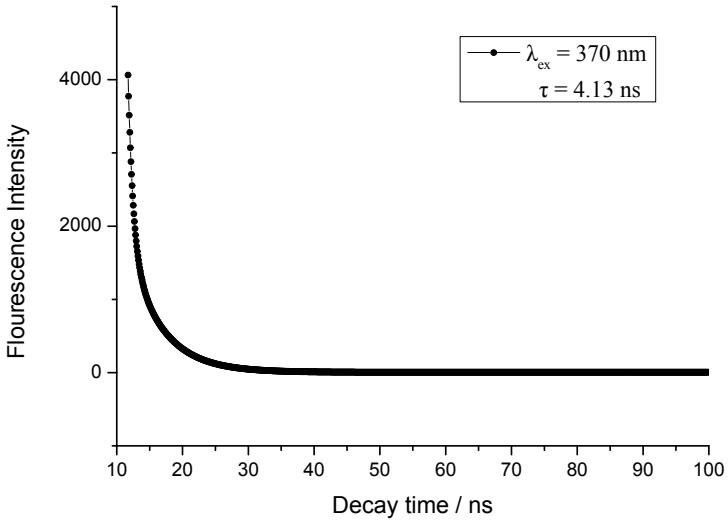


Fig. S14 Fluorescence decay curve of **2-H** (λ_{ex} = 370 nm, monitored at 390 nm) in CH_2Cl_2.

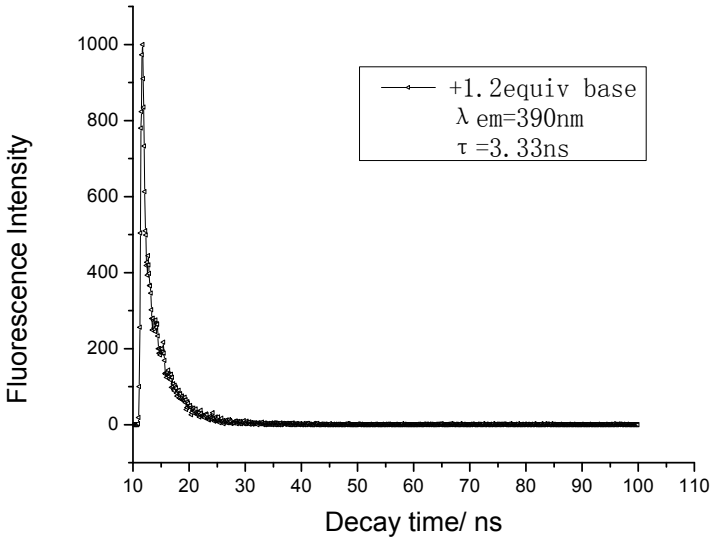


Fig. S15 Fluorescence decay curve of **2** (λ_{ex} = 370 nm, monitored at 390 nm) in CH_2Cl_2.

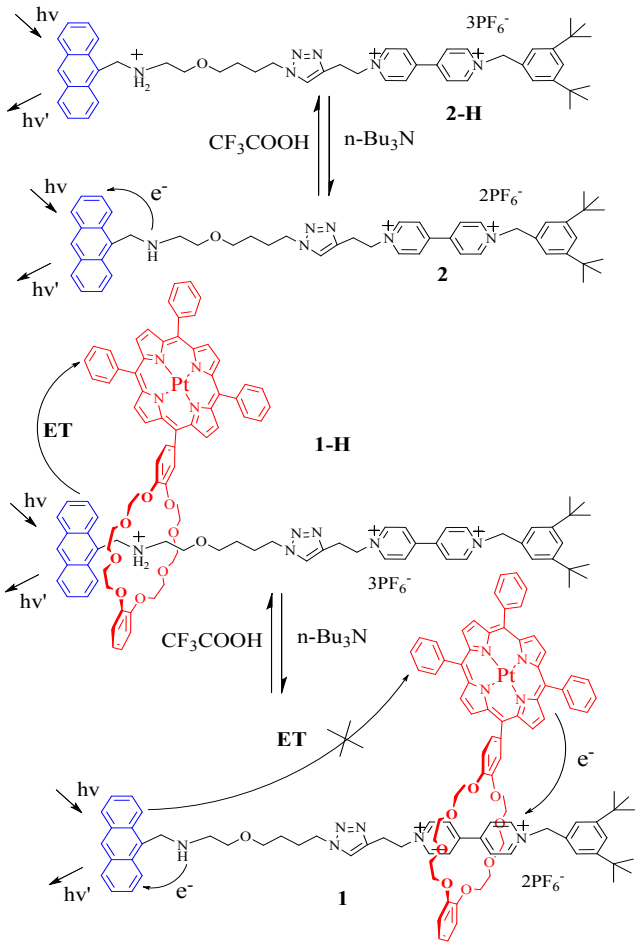


Fig. S16 Photoinduced charge and energy transfer processes (singlet energy transfer process between Anth unit and the porphyrin moiety followed by intersystem crossing from singlet to triplet state in Pt (II) porphyrin) in the dumbbell components **2-H**/**2** and the [2]rotaxanes **1-H**/**1**.

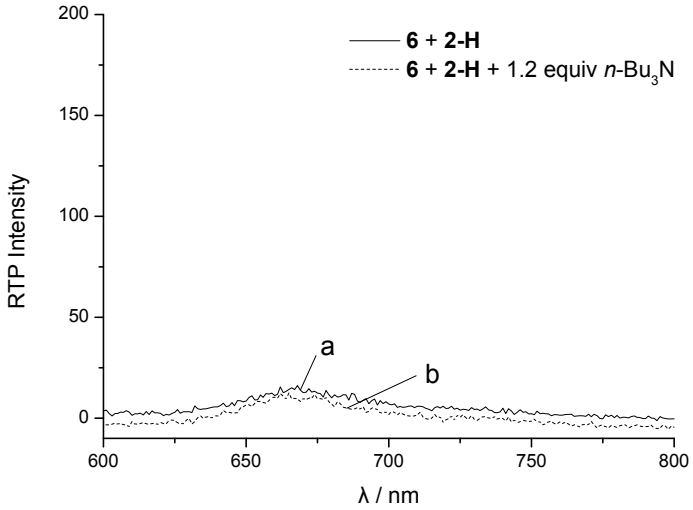


Fig. S17 RTP emission spectra of (a) 1:1 mixture of **6** and **2-H** (solid line) and (b) after addition of *n*-Bu_3N (dot line), 4.0×10^{-6} mol/L, λ_{ex}= 370 nm.

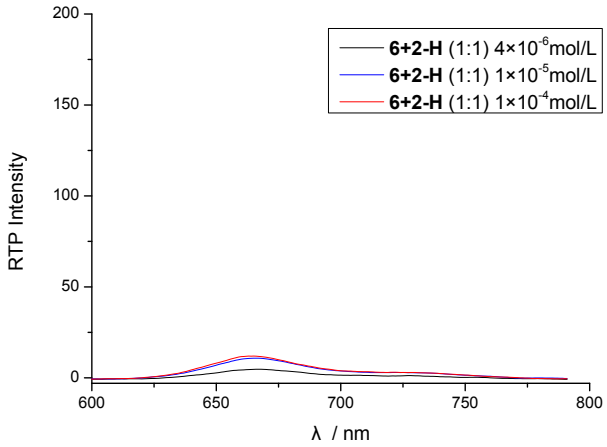


Fig. S18 RTP emission spectra of a mixture of **6** and **2-H** in different concentrations at 298K (λ_{ex} = 370 nm).

We added more control experiments (**2-H**+**6** in different concentrations) shown in Fig. S18. The mixture of **2-H** and **6** showed weak and negligible RTP emission in the different concentrations (from 4.0×10^{-6}, 1.0×10^{-5} to 1.0×10^{-4} mol/L), which helped to confirm that at low concentrations with no possibility of host-guest complex formation energy transfer does not take place.

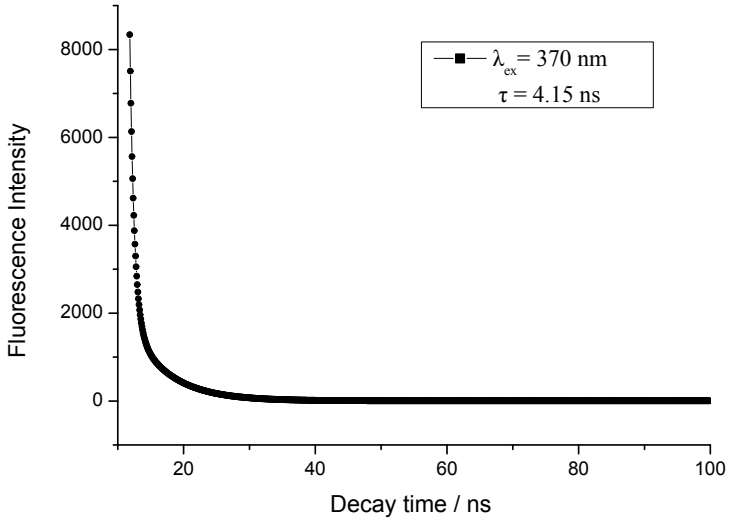


Fig. S19 Fluorescence decay curve of **2-H** and **6** (λ_{ex} = 370 nm, monitored at 390 nm, 5×10^{-5} mol/L) in CH_2Cl_2.

We have done one more control experiment, in which the fluorescence lifetimes of both the dumbbell compound **2-H** and the mechanical mixture of **2-H** and **6** were tested. In this mechanical mixing system, the intermolecular distance between Anth and the porphyrin units was relatively far than the one in [2]rotaxane **1-H**. The fluorescence lifetime of the mechanical mixture of **2-H** and **6** (4.15 ns, Fig. S19) was similar with the one of **2-H** (4.13 ns, Fig. S14) without obvious change in low concentration (5×10^{-5} mol/L), which helped to confirm that the reduced fluorescence lifetime of the Anth emission in **1-H** was attributed to energy transfer, and the energy transfer did not take place at low concentrations with no possibility of host-guest complex formation in the mechanical mixture of **2-H** and **6**.

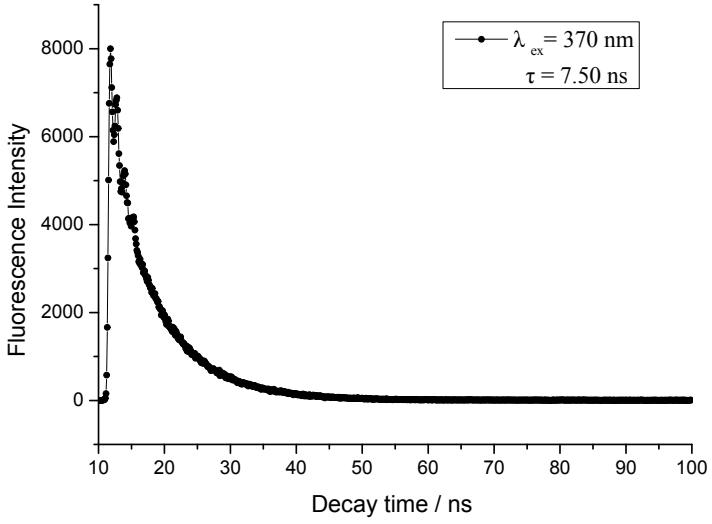


Fig. S20 Fluorescence decay curve of **4** (λ_{ex} = 370 nm, monitored at 390 nm) in CH_2Cl_2.

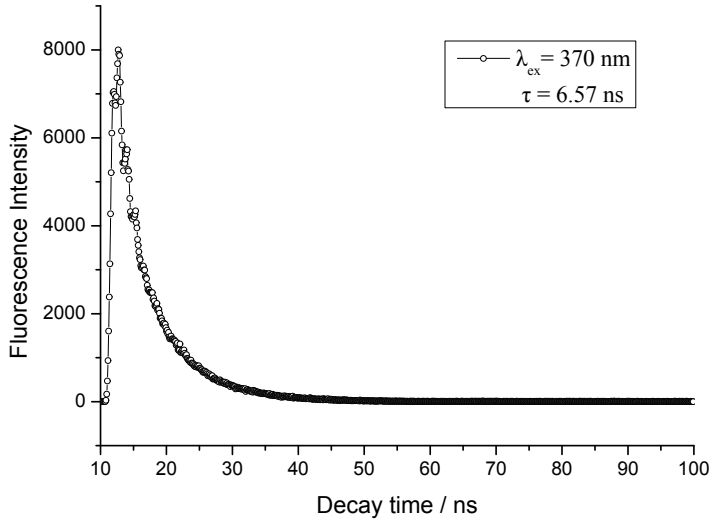


Fig. S21 Fluorescence decay curve of a mixture of **4** and **6** (1:1) (λ_{ex} = 370 nm, monitored at 390 nm) in CH_2Cl_2.

We also did another control experiment, in which the fluorescence lifetimes of both the Anth-containing **4** and the mixture of **4** and the macrocycle **6** (1:1, partially forming pseudorotaxane) were tested and shown in Fig. S20 and S21. The fluorescence lifetime of **4** is about 7.50 ns (λ_{ex} = 370 nm, monitored at 390 nm). While after complexation included by the Pt (II) porphyrin-containing macrocycle **6**, the lifetime reduced to 6.57 ns (λ_{ex} = 370 nm, monitored at 390 nm). This similar decrease effect of lifetime should be attributed to the energy transfer from Anth to the porphyrin moieties in this simple control experiment excluding other potential effect like the possible electron transfer from Anth to 4,4'-bipyridinium ($Bpym^{2+}$) unit in [2]rotaxane **1** (see: *J. Am. Chem. Soc.* 1998, **120**, 11932). This control experiment should be also helpful to explain the point that 'the reduced fluorescence lifetime of the Anth emission in **1-H** is attributed to energy transfer'.

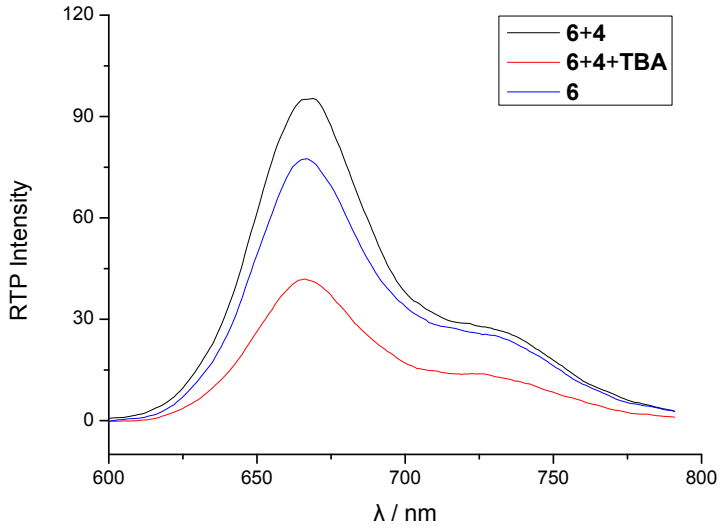


Fig. S22 RTP emission spectra of (a) **6** (blue line), (b) a mixture of **6** and **4** (1:1, black line), and (c) after addition of tributylamine (**TBA**) in the mixture of **6** and **4** (1:1, red line) at 298 K (4×10^{-6}mol/L, λ_{ex} = 370 nm).

About varying the distance between the ammonium station and the anthracene moiety and the spacer between the bipyridinium and ammonium stations, an extra control experiment was designed and carried out, in which the RTP emission of the Pt (II) porphyrin-containing macrocycle **6**, the mixture of **6** and Anth species **4**, and the deprotonated mixture of **6** and **4** were tested. The RTP emission of **6** showed moderate emission intensity (Fig. S22), while the mixture of **6** and Anth species **4** showed an enhanced RTP emission intensity. This enhancement should be due that the energy transfer process from the Anth unit in **4** to the Pt (II) porphyrin moiety in **6** probably occurred in the mixing **6** and **4** system, in which the distance between **6** and **4** was close in the pseudorotaxane complex formed by them. After addition of tributylamine (**TBA**) in the mixture of **6** and **4**, the complexation between **6** and **4** was broken and the distance between Anth and Pt (II) porphyrin became relatively further, thus the RTP emission intensity decreased as expected (Fig. S22).

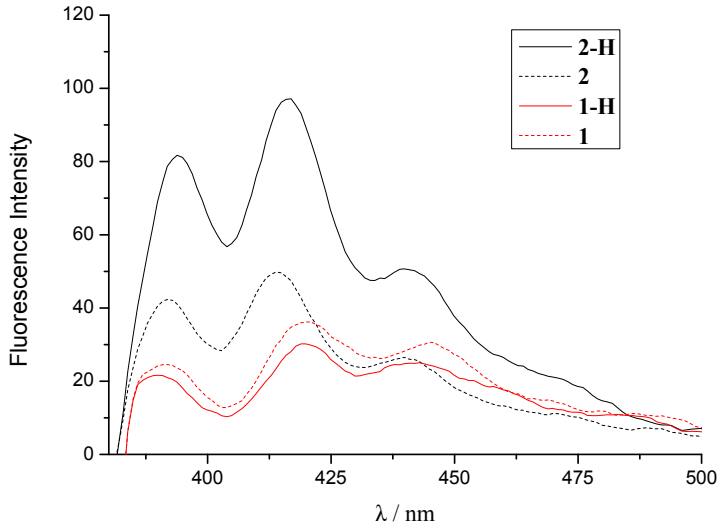


Fig. S23 Fluorescence spectra of the [2]rotaxanes **1-H**/**1** (red, solid/dash lines) and the dumbbell components **2-H**/**2** (black, solid/dash lines), Excitation was performed in the Anth band at 370 nm, 1.0×10^{-5} mol/L.

The fluorescence data (Fig. S23) were repeated under the same conditions as RTP as suggested. The change trends of their intensity were similar with the ones in DCM in spite of some differences of the peak looks. These data were added in the SI of the revised version just for comparation, since usually the fluorescence tests were done in pure solvent while the presence of SDS and Na_2SO_3 used to get better RTP emission signals.

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