Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Effect of the resorcin[4]arene host on the catalytic epoxidation of Mn(III)-based resorcin[4]arene–metalloporphyrin conjugate

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Contents

Synthesis of RC, RCP, and metal derivatives of RCP:[1]

Cavitand resorcin[4]arene (RC).

Octol-resorcin[4]arene (5 g, 5.5 mmol) was dissolved in dimethylformamide (DMF) (55 mL) in a sure-sealed tube. Potassium carbonate (12 g, 88 mmol) was added and stirred for 0.5 h. Bromochloromethane (7.7 mL, 88 mmol) was then added at room temperature. The reaction mixture was sealed and immersed in a preheated oil bath at 80 °C for 24 h. The reaction mixture was poured into ice water and the white solid was collected by suction filtration. Yield: 4.9 g (94 %); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.92 t, 12H, J = 6.80 Hz), 1.37 (m, 32H), 2.00 (s, 12H), 2.22 (q, 8H), 4. 28 (d, 4H, J = 7.2 Hz), 4.78 (t, 4H, J = 8.0 Hz), 5.91 (d, 4H, J = 6.8Hz), 7.00 (s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$), δ: 10.3, 14.1, 22.7, 27.9, 29.2, 30.1, 31.8, 37.0, 98.5, 117.6, 123.6, 138.0 153.2.

Porphyrin resorcin[4]arene conjugate (RCP).

Meso-5-(3-Hydroxyphenyl)-10,15,20-(4-tolyl)porphyrin (100 mg, 0.149 mmol) and K_2CO_3 (100 mg, 0.73 mmol) were dissolved in dry DMF (5 mL) in a sealed tube and stirred for 15 min. Monobrominated cavitand resorcin[4]arene, (150.3 mg, 0.149 mmol) was added to the reaction mixture, and the tube was sealed and stirred in an oil bath at 80 °C for one day. The DMF was evaporated and the solid residue was washed with water and dried. The crude product was adsorbed on silica and mounted on a silica column and eluted with chloroform. After the first band was collected and the solvent was removed, it was dried in a vacuum desiccator until a constant weight was obtained. The compound RCP was obtained as a brownish red solid (183 mg, 77% yield). UV–vis spectrum recorded in CH_2Cl_2, λ_{max} (nm) ($\varepsilon \times 10^{-5}$ M^{-1} cm^{-1}): 417 (3.64), 514 (0.134), 549 (0.057), 590 (0.032) and 644 (0.032). FAB mass: $[M-1]^+$ 1599.1; ^{1}H NMR (400 MHz, $CDCl_3$), δ: - 2.79 (s, 2H), 0.89 (t, 12H, J = 6.8 Hz), 1.34 (m, 32H), 1.87 (s, 6H), 1.92 (s, 3H) 2.21 (m, 8H), 2.71(s, 9H), 4. 32 (d, 2H, J = 7.2 Hz), 4. 42 (d, 2H, J = 7.2 Hz) 4.73 (t, 2H, J = 8.0 Hz), 4.81 (t, 2H, J = 8.0 Hz), 5.21 (s, 2H), 5.76 (d, 2H, J = 6.8Hz), 5.97 (d, 2H, J = 6.8 Hz), 6.93 (s, 1H), 6.97 (s, 2H), 7.24 (s, 1H), 7.33 (m, 1H), 7.56 (m, 6H), 7.68 (t, 1H, J = 8.0 Hz), 7.77 (t, 1H, J = 2.0 Hz), 7.91 (d, 1H, J = 7.6 Hz), 8.09 (d, 6H, J = 6.8 Hz), 8.86 (s, 8H); ^{13}C NMR (150 MHz, $CDCl_3$), δ: 10.4, 10.5, 14.1, 14.1, 14.1, 21.5, 22.7, 22.7, 27.9, 28.9, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 30.1, 30.3, 31.8, 31.9, 31.9, 33.8, 37.0, 37.1, 72.1, 98.6, 100.0, 100.3, 110.4, 114.1, 117.1, 122.0, 123.3, 124.1, 124.5, 127.6, 127.7, 127.8, 128.4, 132.9, 132.9, 134.5, 136.3, 137.6, 137.9, 137.9, 138.3, 138.5, 138.6, 139.3, 139.6, 142.7, 153.2, 153.4, 153.7, 153.9, 160.3.

Zinc derivative of porphyrin resorcin[4]arene conjugate (Zn(II)RCP).

The compound RCP (30 mg) was dissolved in chloroform (10 mL), after which zinc acetate (30 mg) in methanol (5 mL) was added to the solution. The mixture was refluxed until the UV–vis spectrum showed no peak at 650 nm. The solvent was then evaporated and the crude product was purified by column chromatography (silica gel, CH_2Cl_2. The compound Zn(II)RCP, a zinc derivative of RCP, was obtained as a brownish red solid (27 mg, >95% yield). UV–vis spectrum recorded in CH_2Cl_2, λ_{max} (nm) ($\varepsilon \times 10^{-5}$ M^{-1} cm^{-1}): 418 (4.64), 546 (0.179) and 586 (0.039); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.92 (t, 12H, J = 6.8 Hz), 1.36 (m, 32H), 1.91 (s, 6H), 1.96 (s, 3H) 2.26 (m, 8H), 2.75 (s, 9H), 4. 35 (d, 2H, J = 7.2 Hz), 4. 43 (d, 2H, J = 7.2 Hz), 4.74 (t, 2H, J = 8.0 Hz), 4.82 (t, 2H, J = 8.0 Hz), 5.22 (s, 2H), 5.79 (d, 2H, J = 6.8Hz), 5.98 (d, 2H, J = 7.2 Hz), 6.96 (s, 1H), 6.99 (s, 2H), 7.26 (s, 1H), 7.34 (m, 1H), 7.59 (m, 6H), 7.71 (t, 1H, J = 8.0 Hz), 7.82 (s, 1H), 7.95 (d, 1H, J = 7.6 Hz), 8.13 (m, 6H), 9.01 (s, 8H);^{13}C NMR (150 MHz, $CDCl_3$), δ: 10.2, 10.9, 14.3, 14.4, 21.8, 22.9, 22.9, 28.1, 28.2, 29.2, 29.4, 29.6, 29.7, 29.8, 29.9, 29.9, 29.9, 30.3, 30.4, 31.8, 32.0, 32.1, 32.2, 34.1, 37.2, 61.6, 98.4, 99.9, 113.9, 114.3, 117.3, 117.6, 120.2, 124.3, 127.5, 131.8, 132.2, 132.3, 134.6, 137.4, 137.4, 137.5, 137.9, 138.2, 138 9, 140.0, 150.1, 150.5, 150.6, 150.6, 153.5, 153.7, 154.3, 156.9.

Single crystal X-ray diffraction:

*X-Ray structure of cavitand resorcin[4]arene (**RC**):*

Singles crystals of cavitand resorcin[4]arene (**RC**) suitable for single crystal X-ray diffraction were grown from solvent diffusion method. **RC** (50mg), dissolved in 1 mL ethylacetate was taken in a small vial with a narrow opening and kept inside a big vial containing 10ml Hexane. Hexane was allowed to diffuse into the RC solution slowly and within 10 days suitable single crystals were grown. The single crystal data collections were made on a Rigaku R-AXIS RAPID diffractometer using crystalclear software package at -123 ^{o}C. The structure was solved and refined using the Bruker SHELXTL Software Package (Structure solution program- SHELXS-97 and Refinement program- SHELXL-97). The X-ray molecular structure of RC is shown in Figure S1.

*X-Ray structure of cavitand resorcin[4]arene-pyridine inclusion complex (**RC-PY**):*

Singles crystals of **RC-PY** suitable for single crystal X-ray diffraction were grown from solvent diffusion method. RC (50mg), dissolved in 1 mL ethylacetate containing 2drops of pyridine was kept in a small vial with a narrow opening and kept inside a big vial containing 10ml Hexane. Hexane was allowed to diffuse into the RC solution slowly and within 10 days suitable single crystals in which pyridine are trapped within RC framework were grown. The single crystal data collections were made on a Rigaku R-AXIS RAPID diffractometer using crystalclear software package at -123 ^{o}C. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL-97[2]. The X-ray molecular structure of RC-PY is shown in Figures S2-3 and a detail of the crystal lattice in Figure S4.

*X-Ray structure of cavitand resorcin[4]arene-styrene inclusion complex (**RC-STY**):*

Singles crystals of RCSTY suitable for single crystal X-ray diffraction were grown from solvent diffusion method. RC (50mg), dissolved in 1 mL acetone containing 2drops of styrene was kept in a small vial with a narrow opening and kept inside a big vial containing 10ml Hexane. Hexane was allowed to diffuse into the RC solution slowly and within 10 days suitable single crystals in which styrene are trapped within RC framework were grown. The single crystal data collections were made on a Rigaku R-AXIS RAPID diffractometer using crystalclear software package at -123 ^{o}C. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. The X-ray molecular structure of RC-STY is shown in Figures S5-6 and a detail of the crystal lattice in Figure S7.

*X-Ray structure of Porphyrine-resorcin[4]arene conjugate (**RCP**).*

Singles crystals of RCP suitable for single crystal X-ray diffraction were grown from solvent evaporation method. RCP (20mg), dissolved in 1 mL ethylacetate: cyclehexane mixture (1:1 v/v) was kept in a small vial with a narrow opening and evaporated off the solvent very slowly. Within 2 weeks suitable single crystals were grown. However attempts to grow bigger crystals were not successful as they are found to be deteriorated. The single crystal data collections were made on a Rigaku R-AXIS RAPID diffractometer using crystalclear software package at -123 ^{o}C. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. . The X-ray molecular structure of RCP is shown in Figure S8 and a detail of the crystal lattice in Figure S9.

Table S1: Crystal data and refinement parameters obtained from the structural analysis of **RC-PY**, **RC-STY** and **RCP.**

Compound	**RCPY**	**RCSTY**	**RCP**
Crystal size /mm	0.20X0.10X 0.03	0.20X0.20X0.15	0.20X0.15X0.05
Crystal Shape	Chunk	Block	Platlet
Formula weight	$C_{65}H_{85}NO_8$	$C_{68}H_{88}O_8$	$C_{111}H_{122}N_4O_{11}$
Crystal system	orthorhombic	orthorhombic	triclinic
Space group(no.)	Pnma (#62)	Pnma (#62)	P-1 (#2)
T/^{o}C	-123	-123	-123
a/Å	23.223(2)	23.220(2)	15.83(1)
b//Å	20.341(2)	20.5223(4)	16.00(1)
c/Å	12.1702(6)	12.0874(3)	20.20(2)
α/deg	90	90	94.81(2)
β/deg	90	90	91.04(2)
γ/deg	90	90	116.09(2)
V/ Å^3	5748.7(6)	5759.9(5)	4569(5)
Z	4	4	2
μ(MOKα) mm^{-1}	0.075	0.076	0.078
ρ_{calcd}/g cm^{-3}	1.165	1.192	1.227
θ_{max}/deg	25.35	27.46	25.03
Reflections collected	16076	54999	31464
Unique reflections	5248	6745	15475
R_{int}	0.1130	0.0435	0.0718
R (I > 2σ)	0.0759	0.0437	0.1085
R (all data)	0.1657	0.0583	0.1936
R_w(all data)	0.2233	0.1247	0.3493
Peak$_{max}$ (e$^-$/Å^3)	0.55 e	0.56	0.60

Figure S1. ORTEP crystal structure of resorcin[4]arene (**RC**).

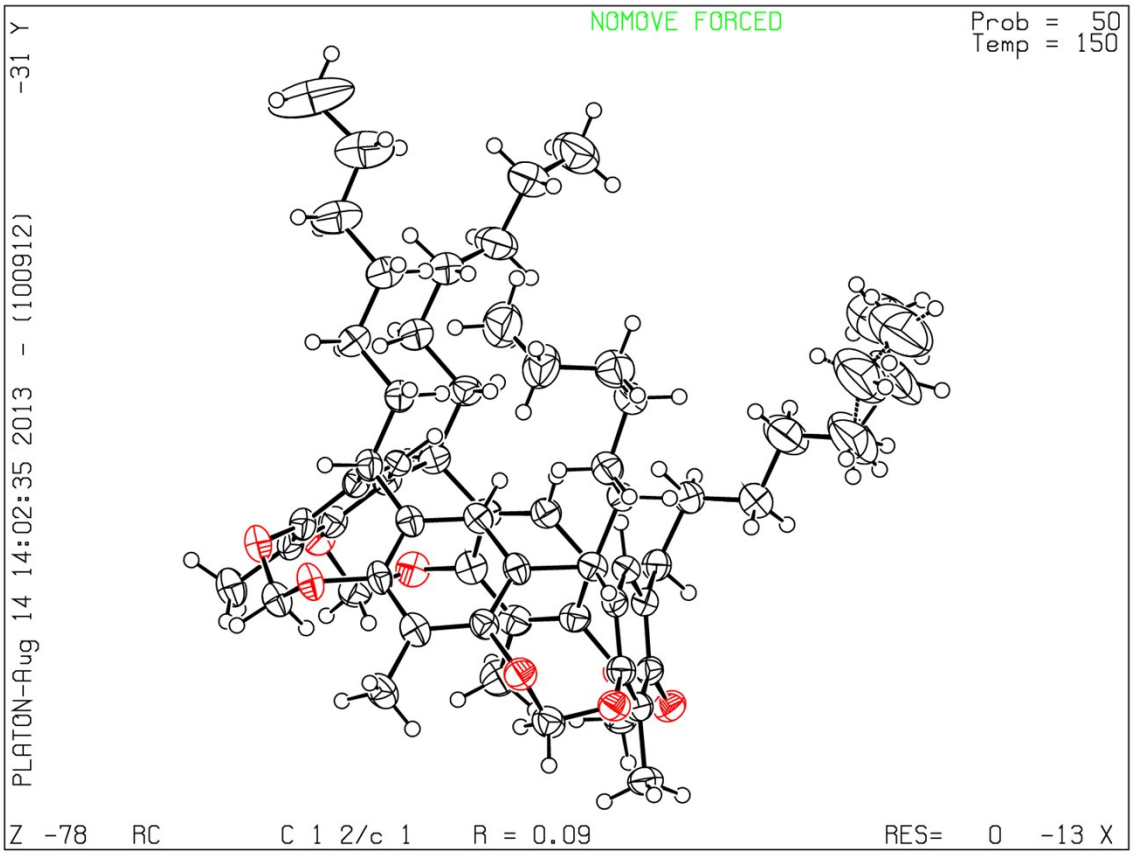
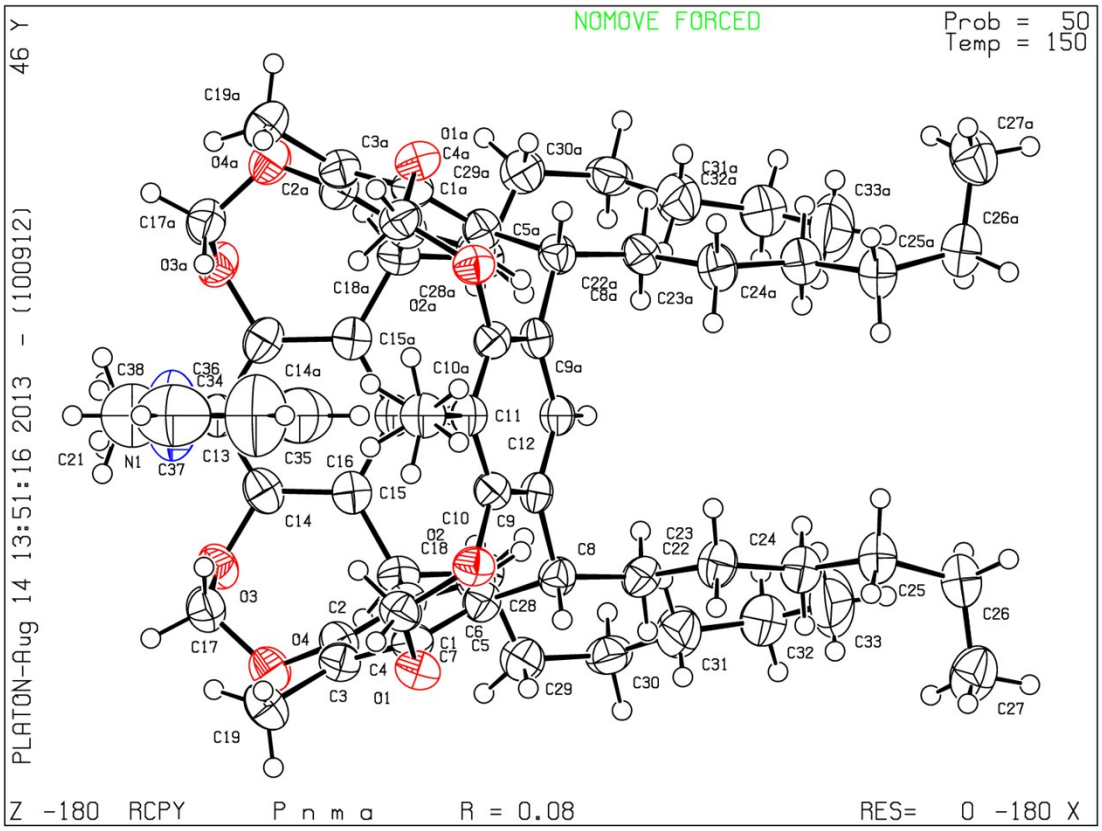


Figure S2. ORTEP crystal structure of inclusion complex **RC-PY**.



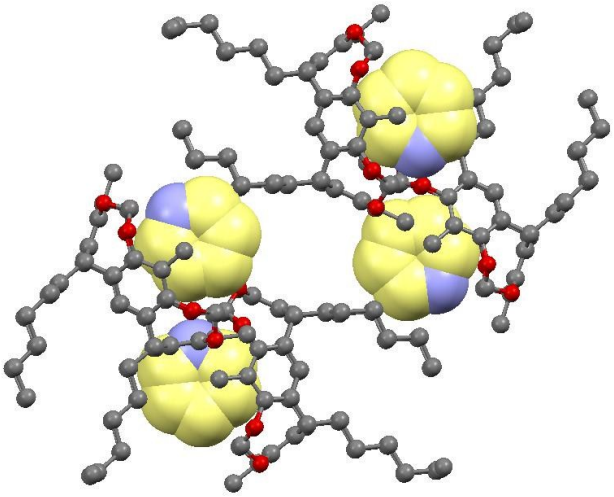


Figure S3. The unit cell of resorcin[4]arene-pyridine inclusion-complex (**RC-PY**)crystals viewing along its b-direction (Color code: red – oxygen and gray- carbon; hydrogen atoms are hided for clarity).

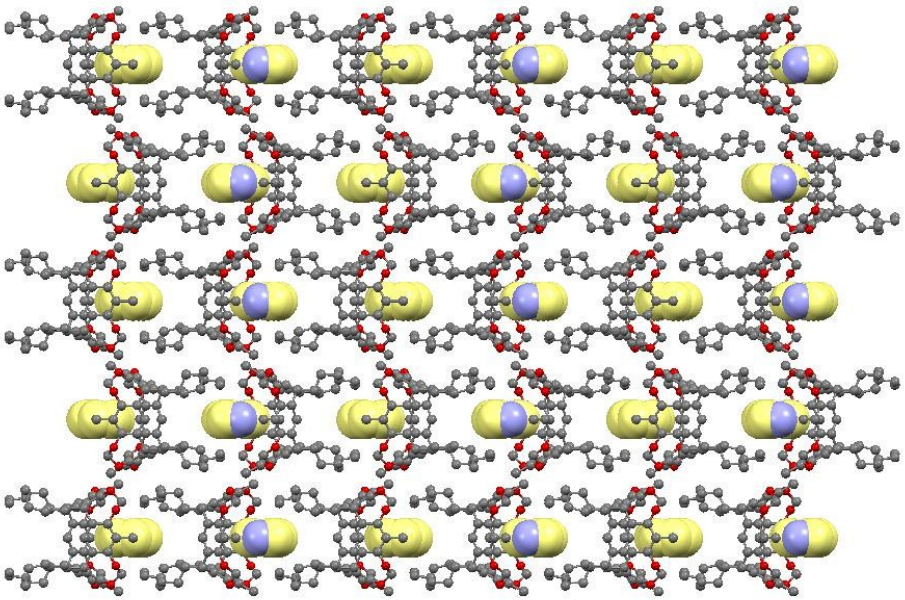
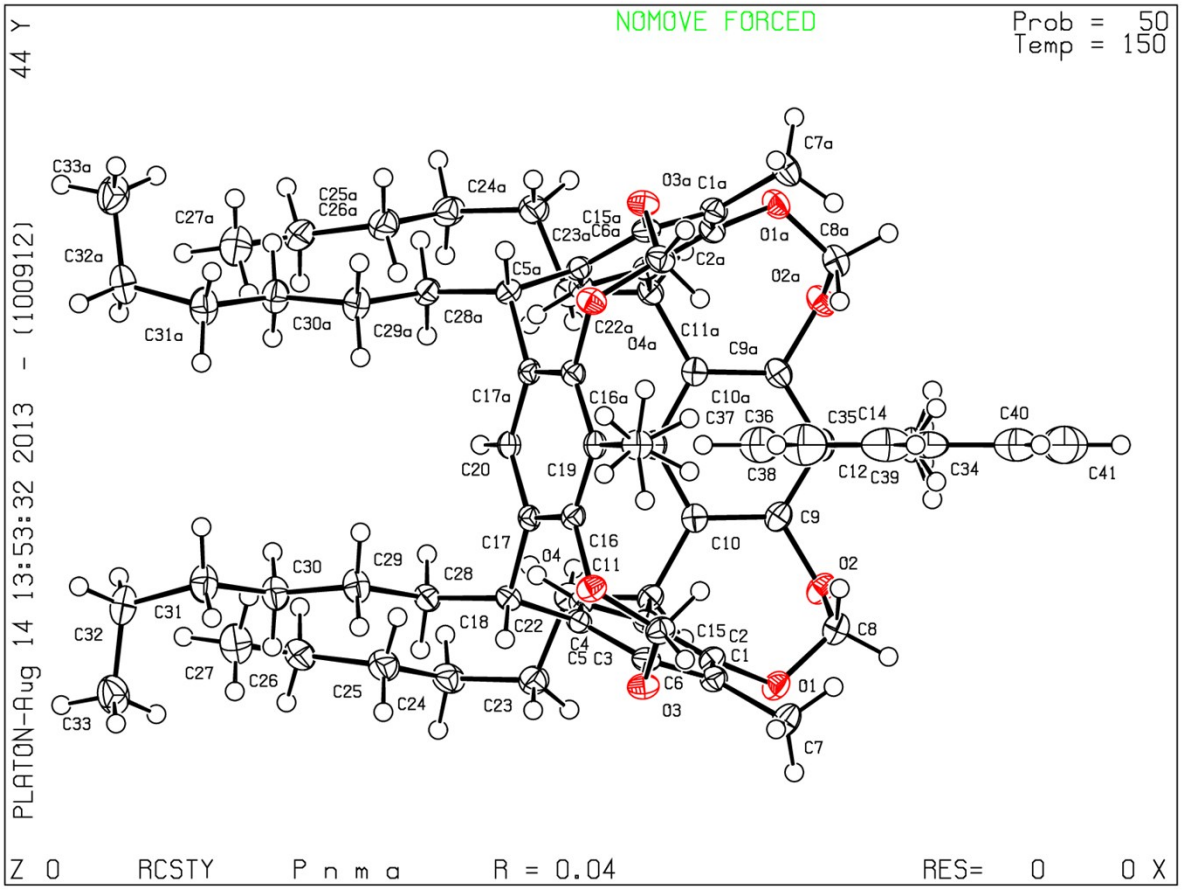


Figure S4. Three-dimensional packing of resorcin[4]arene-pyridine inclusion-complex (**RC-PY**)crystals viewing along its c-direction (hydrogen atoms are hided for clarity).

Figure S5. ORTEP crystal structure of inclusion complex **RC-STY**.



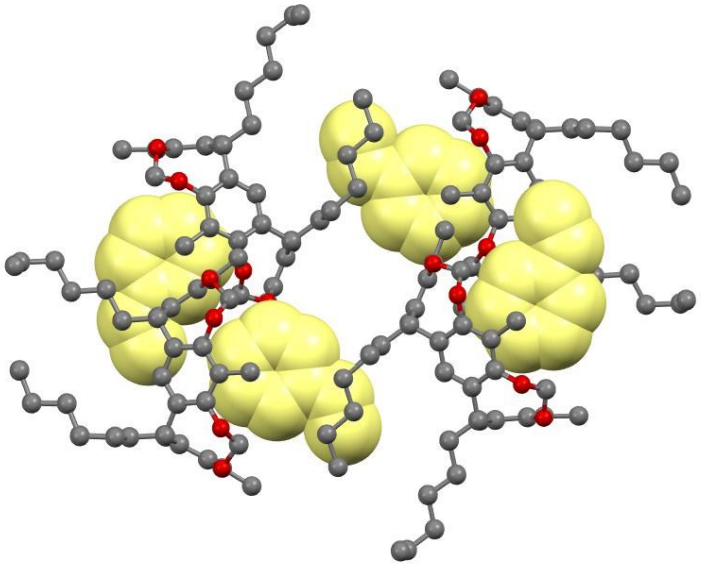


Figure S6. The unit cell of resorcin[4]arene-styrene inclusion-complex (**RC-STY**)crystals viewing along its b-direction (Color code: red – oxygen and gray- carbon; hydrogen atoms are hided for clarity).

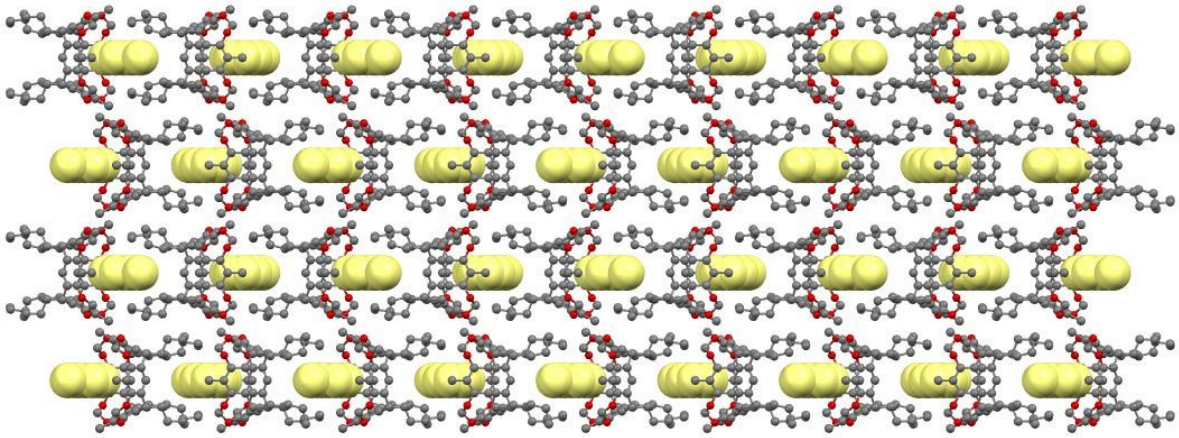
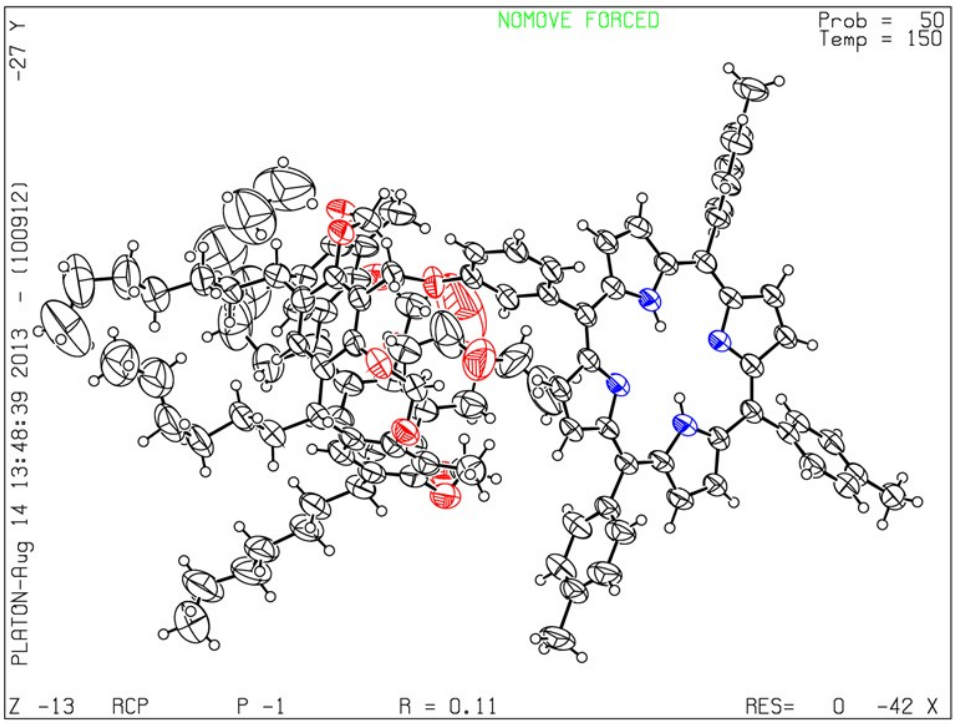


Figure S7. Three-dimensional packing of resorcin[4]arene-styrene inclusion-complex (**RC-STY**)crystals viewing along its c-direction (hydrogen atoms are hided for clarity).

Figure S8. ORTEP crystal structure of **RCP**.



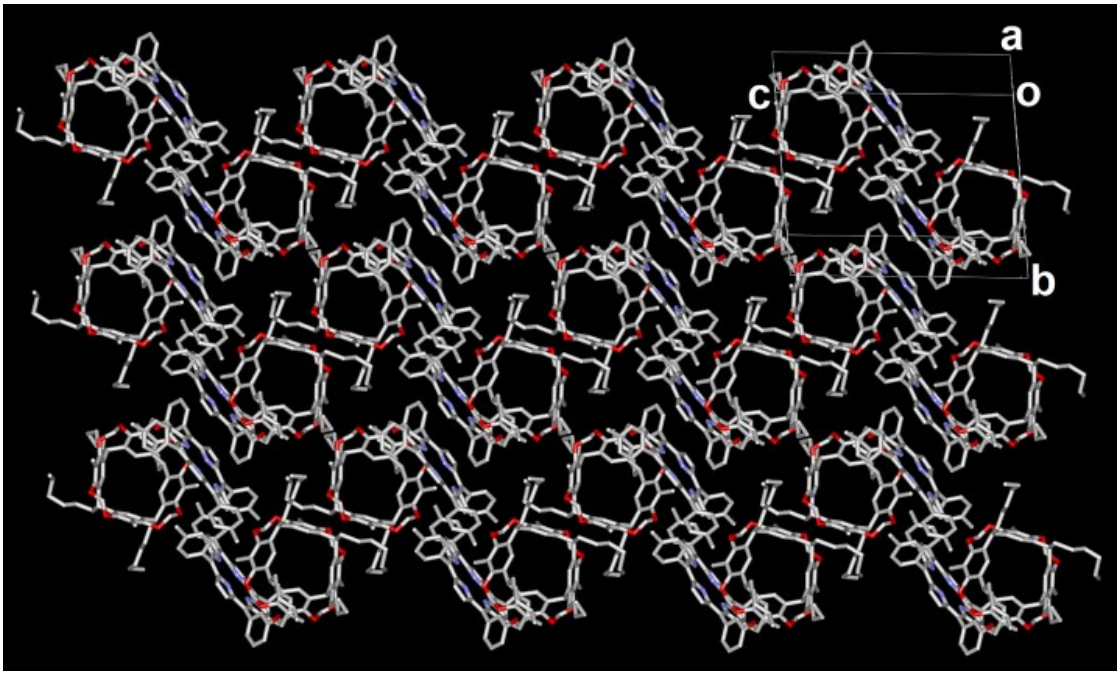


Figure S9. Three-dimensional packing of **RCP** crystals when hydrogen atoms and solvent molecules are hided.

NMR Spectra:

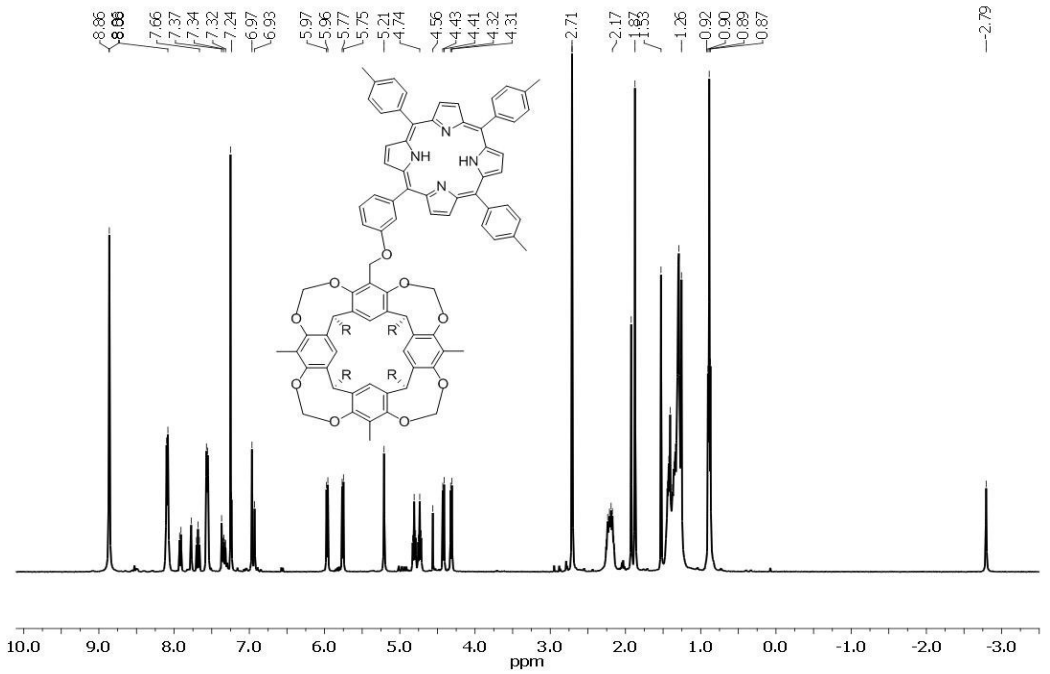


Figure S10: ^{1}H NMR of RCP (from Ref. 1)

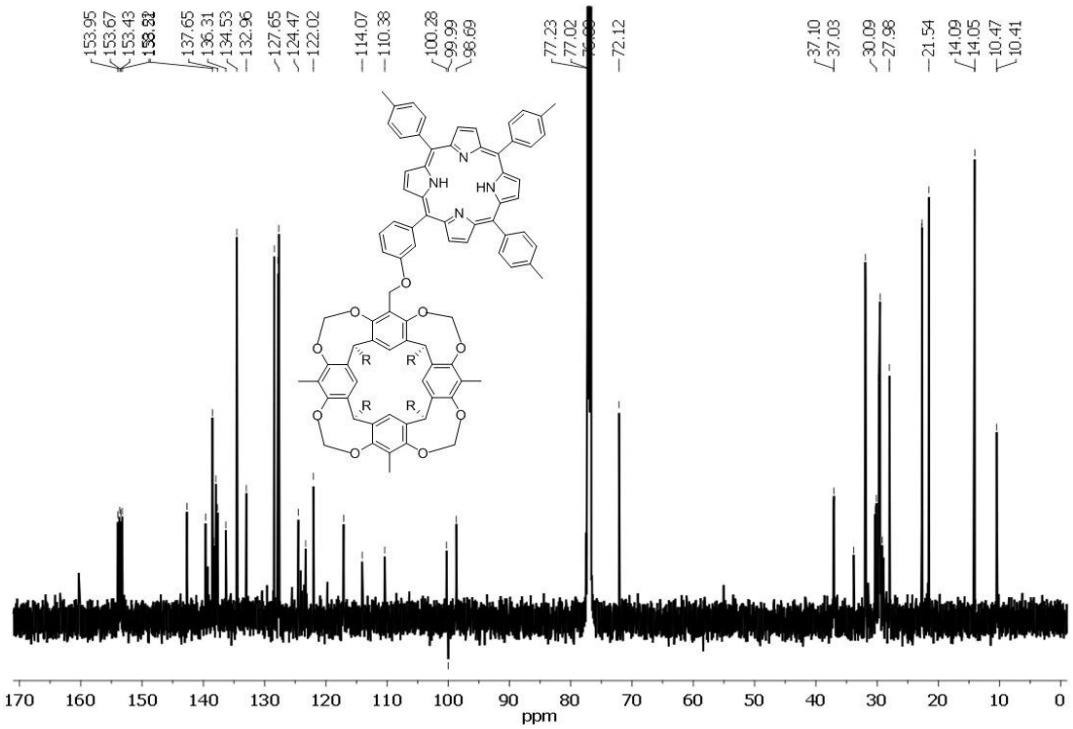


Figure S11. ^{13}C NMR of **RCP.**(Ref. 1)

Mass Spectra:

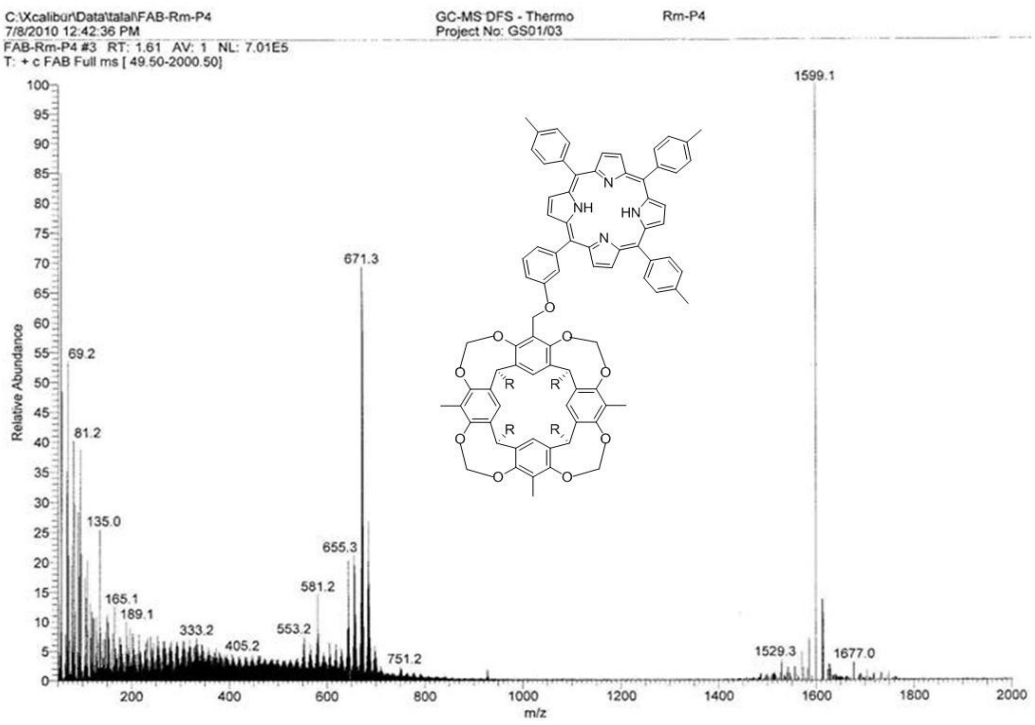


Figure S12: FAB-MS of **RCP** (from Ref. 1)

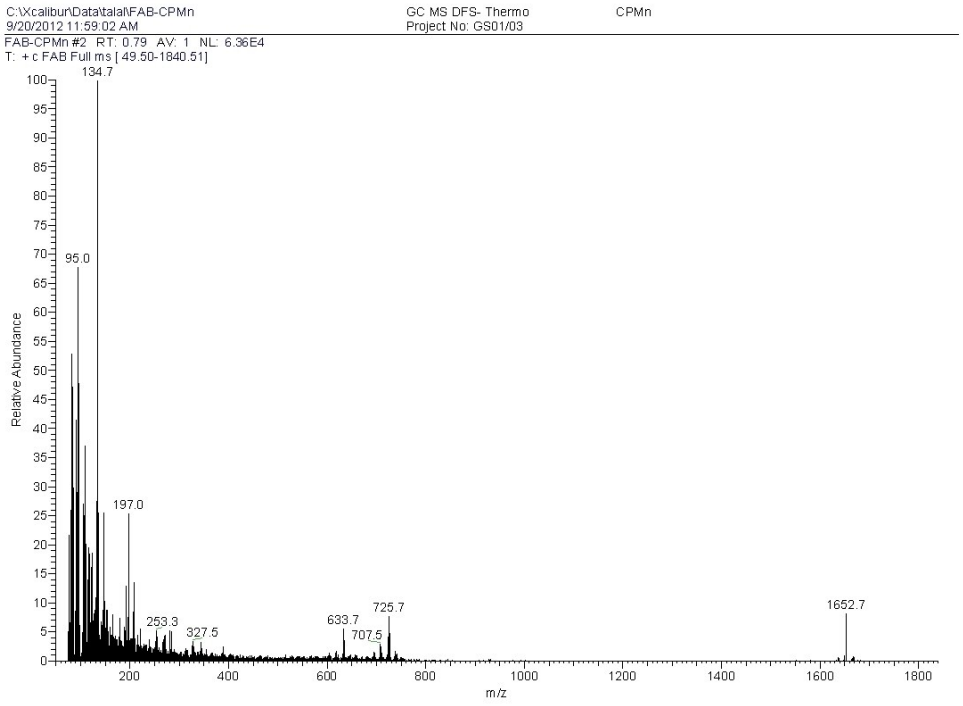


Figure S13: FAB-MS of **MnRCP**.

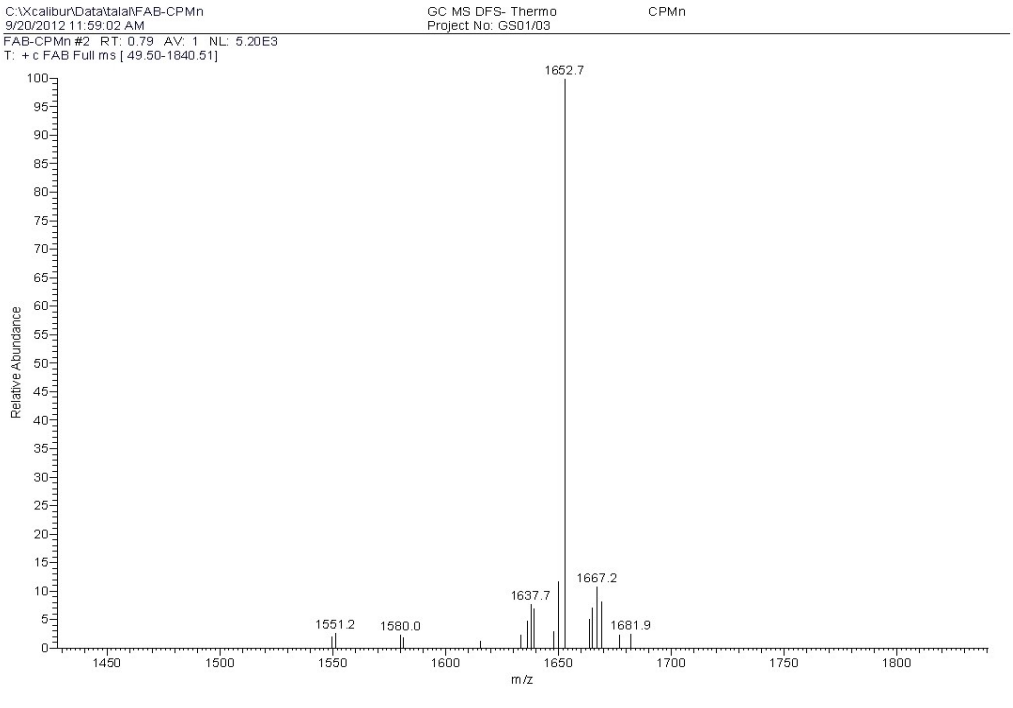


Figure S14: FAB-MS of **MnRCP** (m/z showing above 1000)

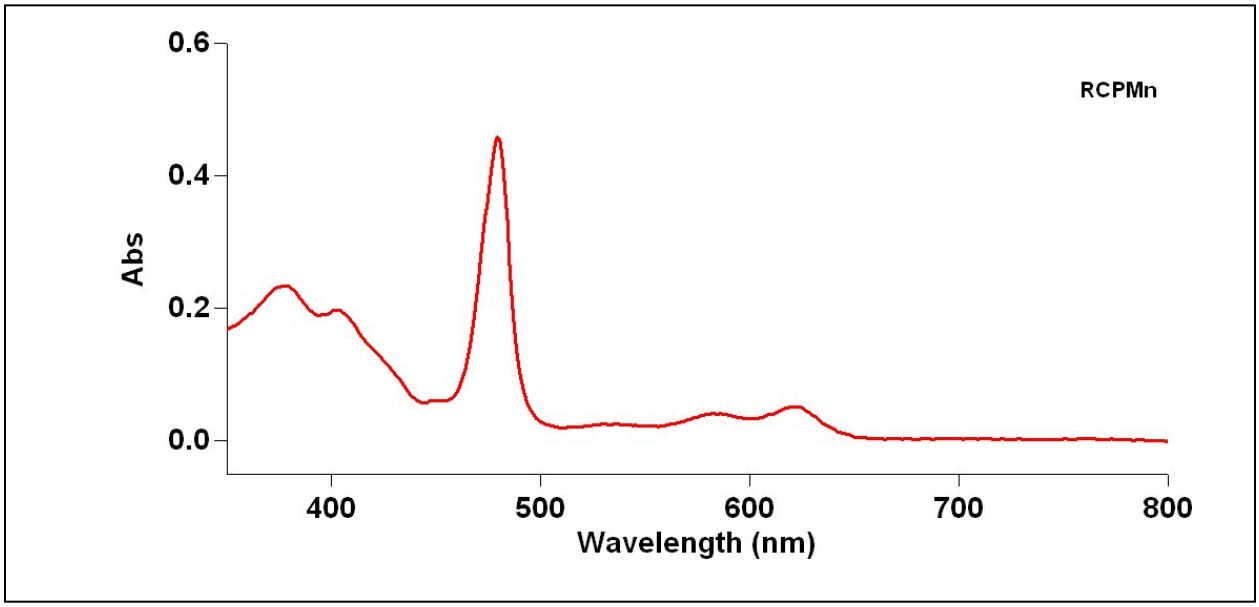


Figure S15: UV-Vis Spectrum of **MnRCP** in CH_2Cl_2.

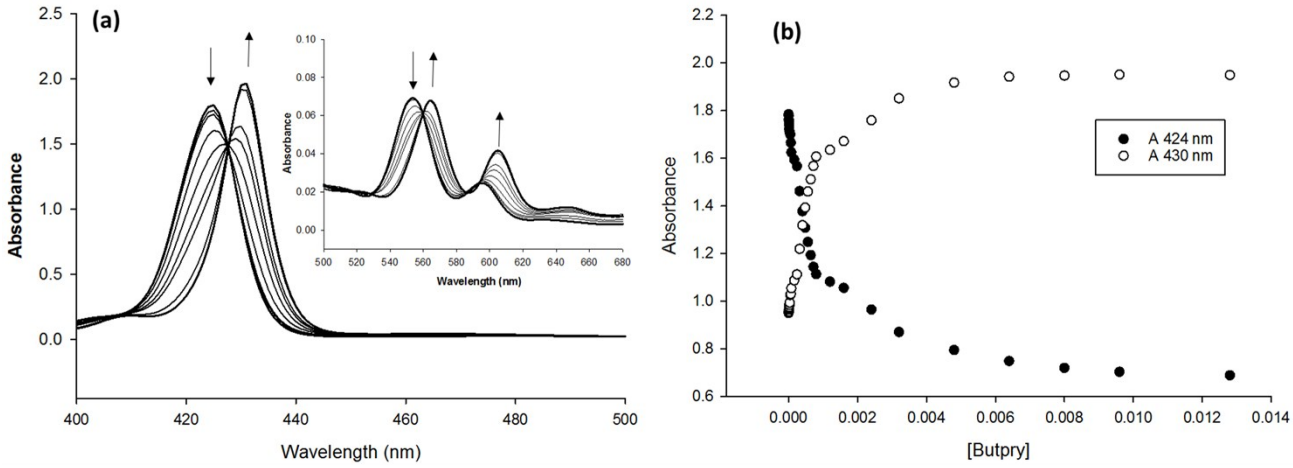


Figure S16. (a) Absorption spectral changes observed in dry chloroform solution of **ZnRCP** (8 μM) by addition of 4-*tert*-butylpyridine (Bupy] (0-10^{-3} M) at 25 ^{0}C. (b) The binding isotherm of the system ZnRCP–4-*tert*-butylpyridine at 424 nm (ஜ) and 430 nm (ᘓ).

References

1. T. F. Al-Azemi, M. Vinodh, *Tetrahedron* 2011, 67, 2585-2590.
2. SHELX97: G. M. Sheldrick, *Acta Cryst*. 2008, A64, 112-122.
3. CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.