Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Template-Free Self-Assembly of molecular Trefoil knotsand 1D metallasupramolecular chain featuring half-sandwich Cp*·Rh building blocks.

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Table of Contents

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General experimental information

All the chemicals were purchased from the commercial companies and used as obtained unless otherwise mentioned. $[Cp^*RhCl_2]_2$ (Cp^* = η5-pentamethyl-cyclopentadienyl) were synthesized according to the previously published procedure[1]. NMR spectra were performed on a Bruker AVANCE I 400 spectrometer at room temperature and referenced to the signal of the residual protonated solvent. Proton chemical shifts are reported relative to the solvent residual peak (δH = 3.31 ppm for CD_3OD), Elemental analyses (C, H, N) were carried out on an Elemental Vario EL III analyzer.

ESI-TOF-MS data of 2-mono.

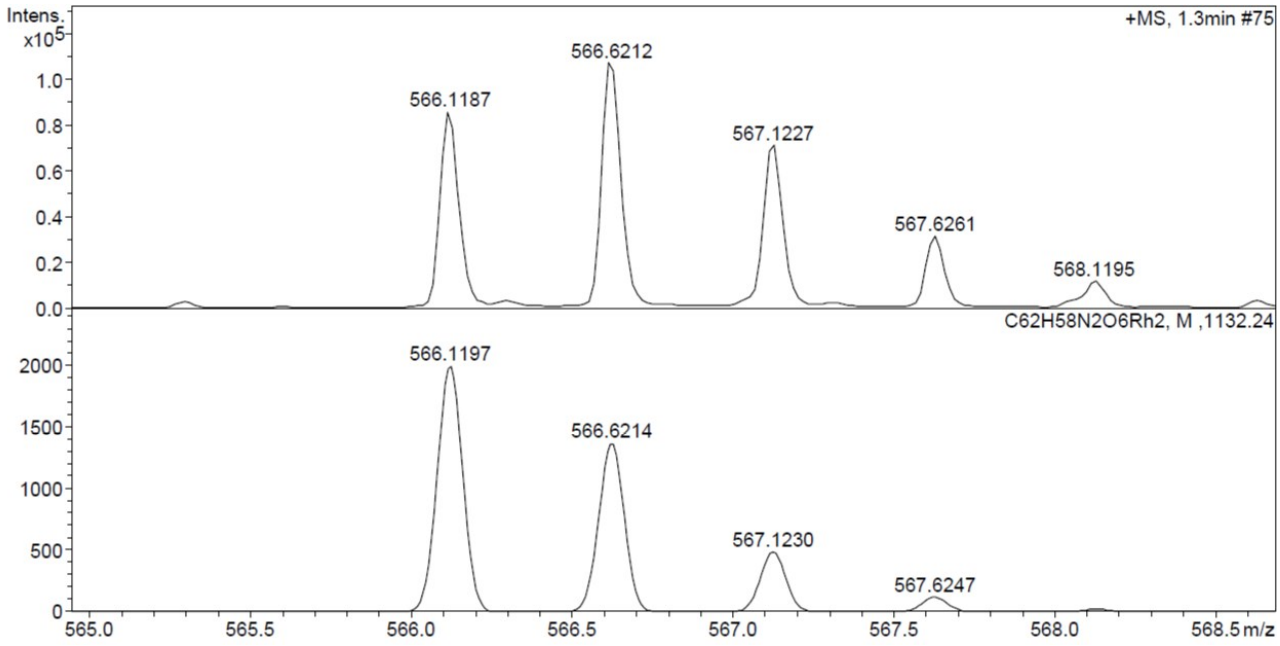

Fig.S1 Calculated (bottom, red) and experimental (top, blue) ESI-TOF-MS

spectrum (2+) of complex **2-mono**.

NMR Spectra

1. Spectra of Ligand L (400 MHz, CD_3OD).

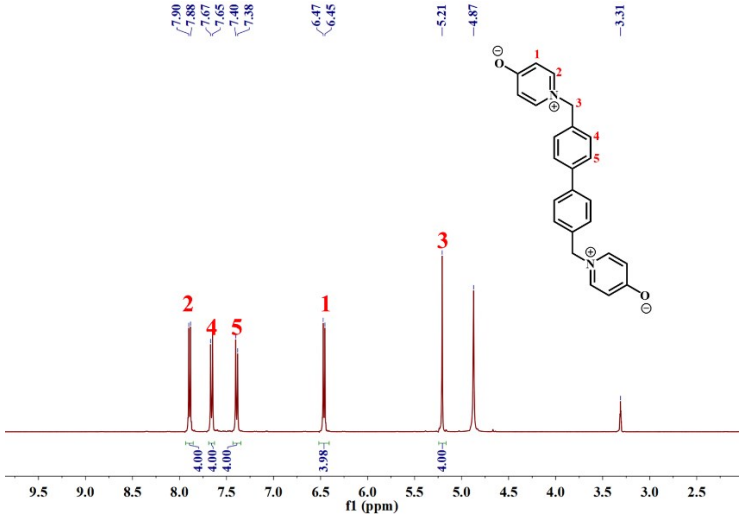

Fig.S2 ^{1}H NMR spectrum of ligand **L**.

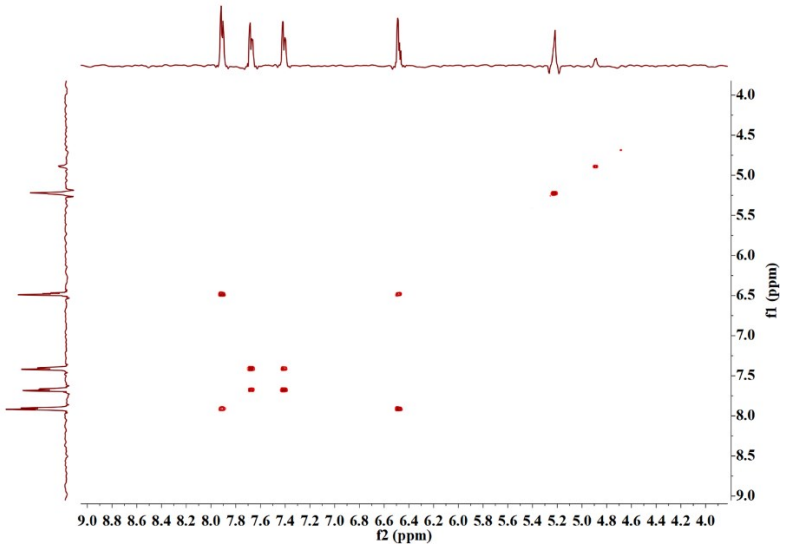

Fig.S3 ^{1}H-^{1}H COSY spectrum of ligand **L**.

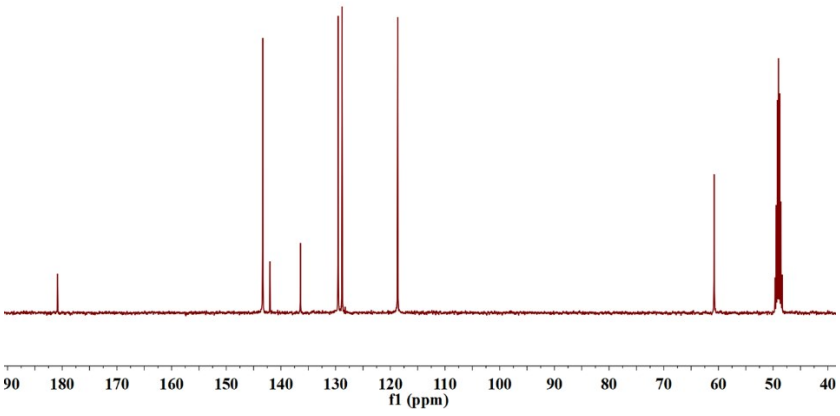

Fig.S4 ^{13}C NMR spectrum of ligand **L**.

2. Spectra of Trefoil knot 1 (400 MHz, CD_3OD).

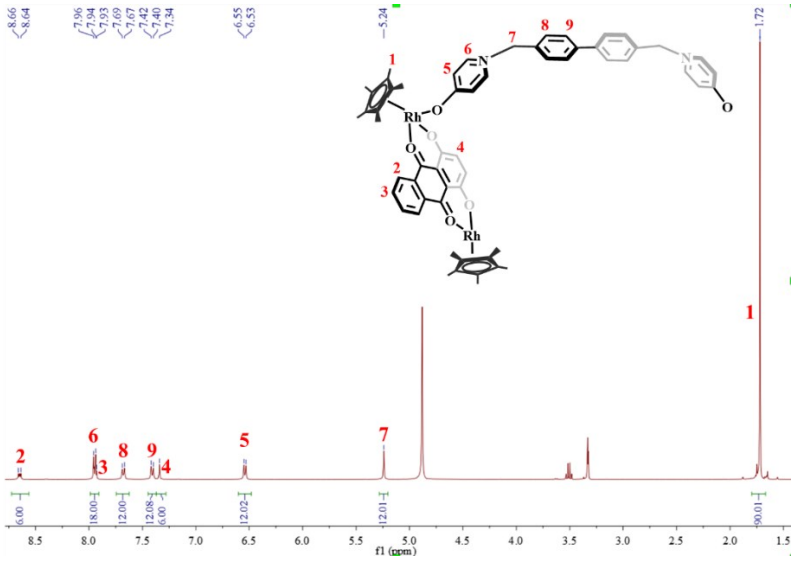

Fig.S5 ^{1}H NMR spectrum of trefoil knot **1**.

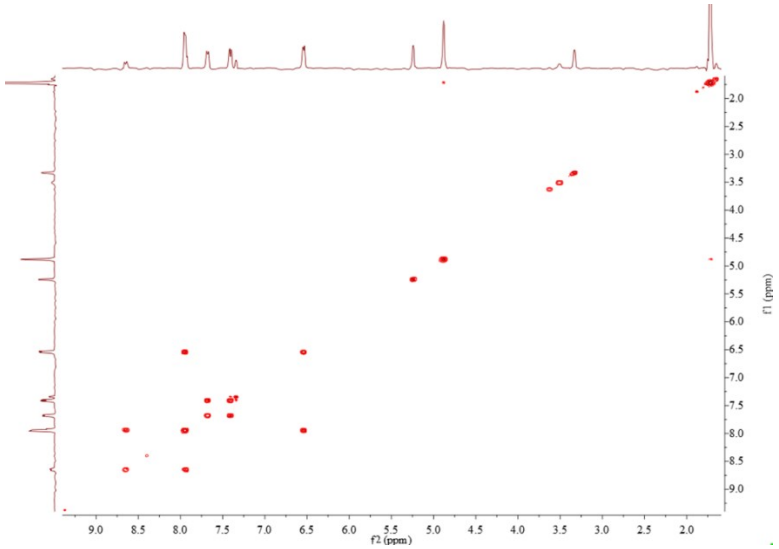

Fig.S6 ^{1}H-^{1}H COSY NMR spectrum of trefoil knot **1**.

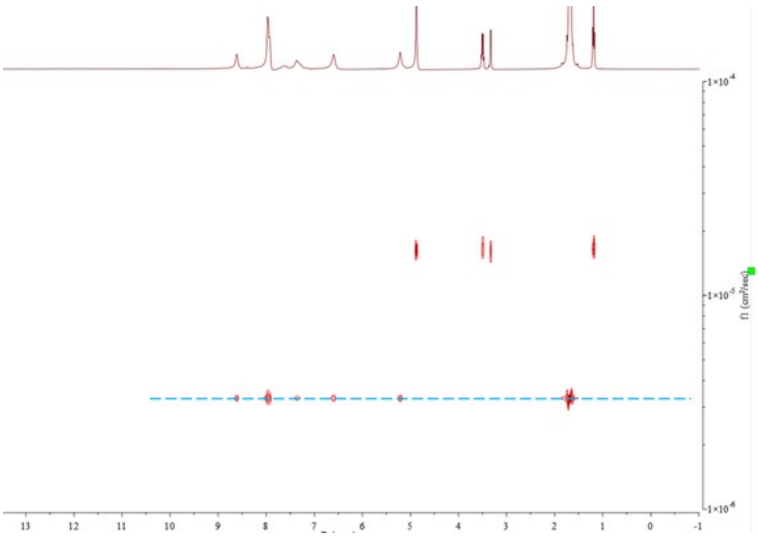

Fig.S7 ^{1}H DOSY NMR of trefoil knot **1**.

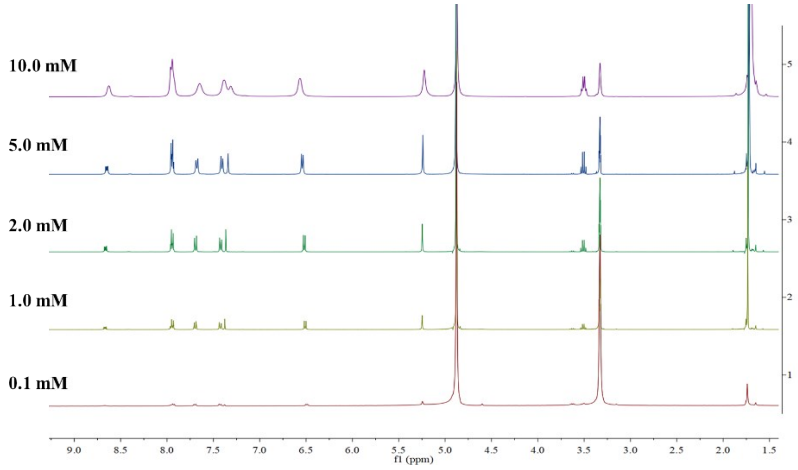

Fig.S8 Dilution experiments of trefoil knot **1** from 10.0 mM to 0.1 mM.

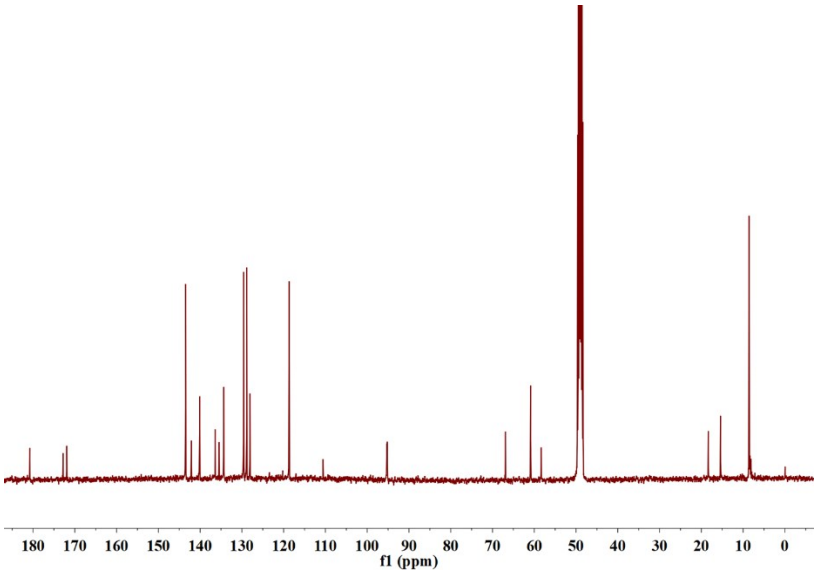

Fig.S9 ^{13}C NMR spectrum of trefoil knot **1**.

3. Spectra of Trefoil knot 2 (400 MHz, CD_3OD).

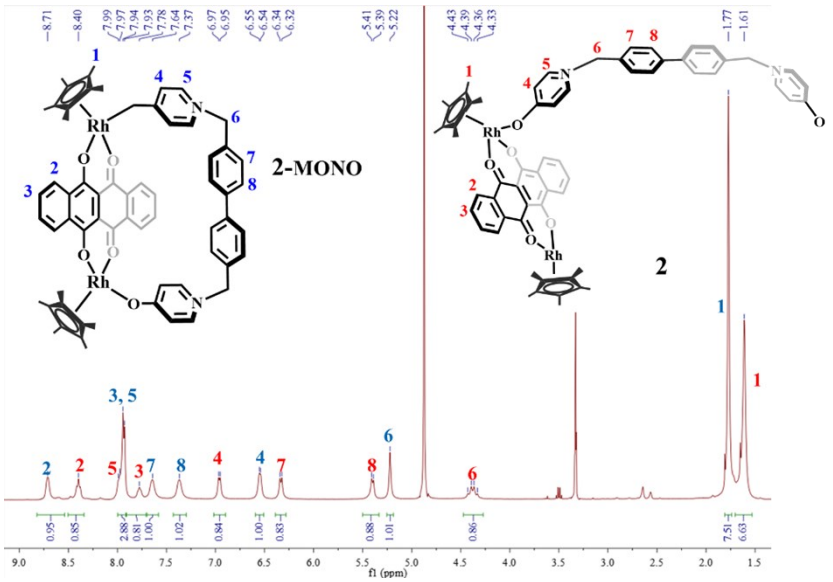

Fig.S10 ^{1}H NMR spectrum of trefoil knot **2** and **2-MONO**.

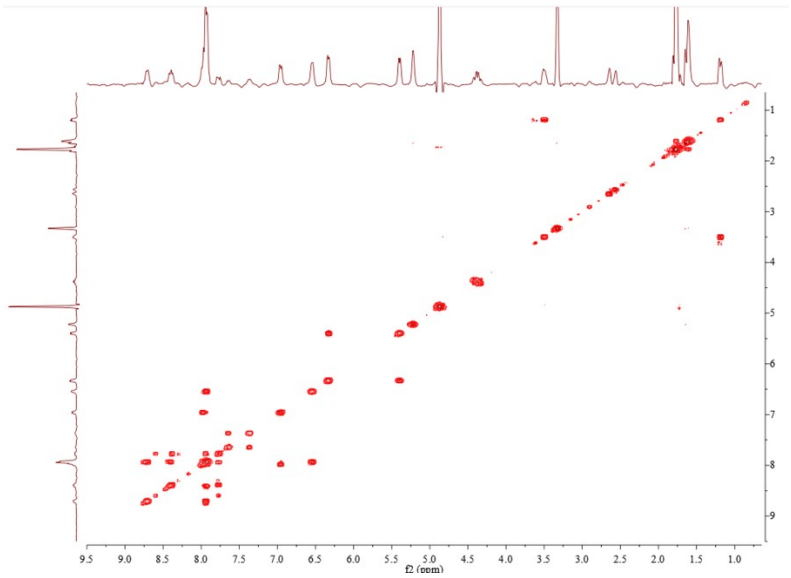

Fig.S11 ^{1}H-^{1}H COSY NMR spectrum of trefoil knot **2** and **2-MONO**.

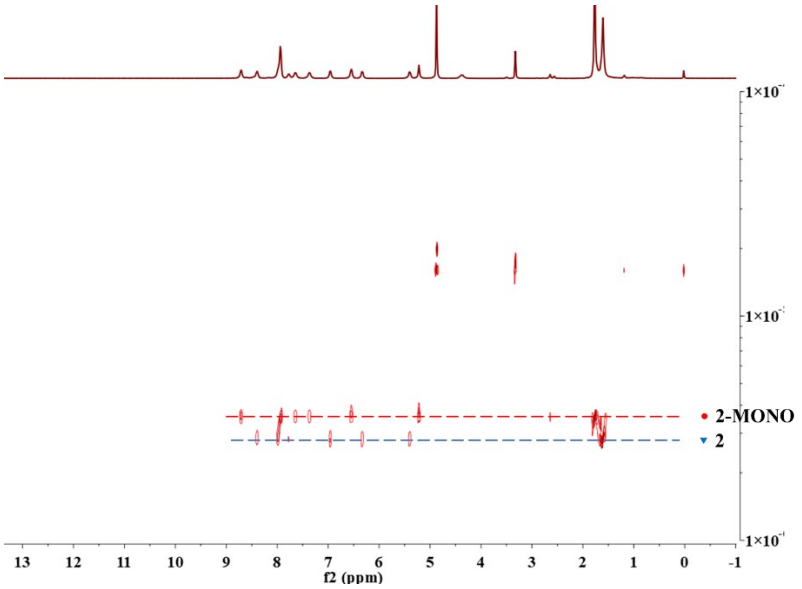

Fig.S12 ^{1}H DOSY NMR of trefoil knot **2** and **2-MONO.**

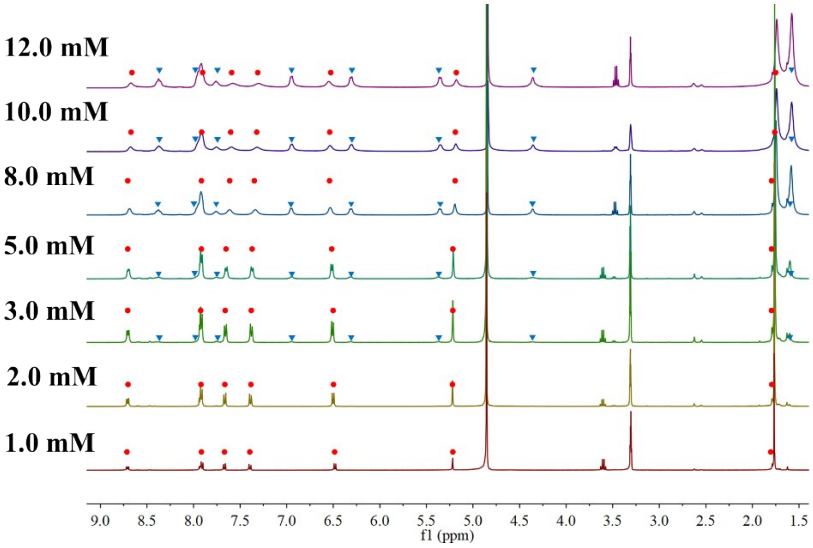

Fig.S13 Dilution experiments of trefoil knot **2** from 10.0 mM to 1.0 mM.

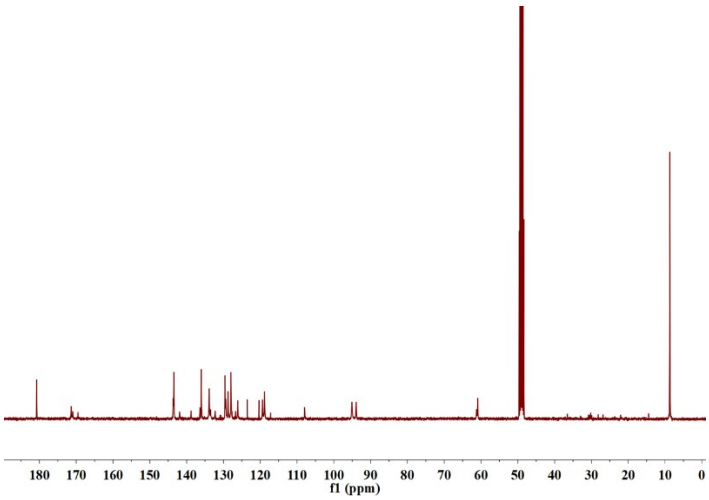

Fig.S14 ^{13}C NMR spectrum of trefoil knot **2**.

4. Spectra of one-dimension chain 3 (400 MHz, CD_3OD).

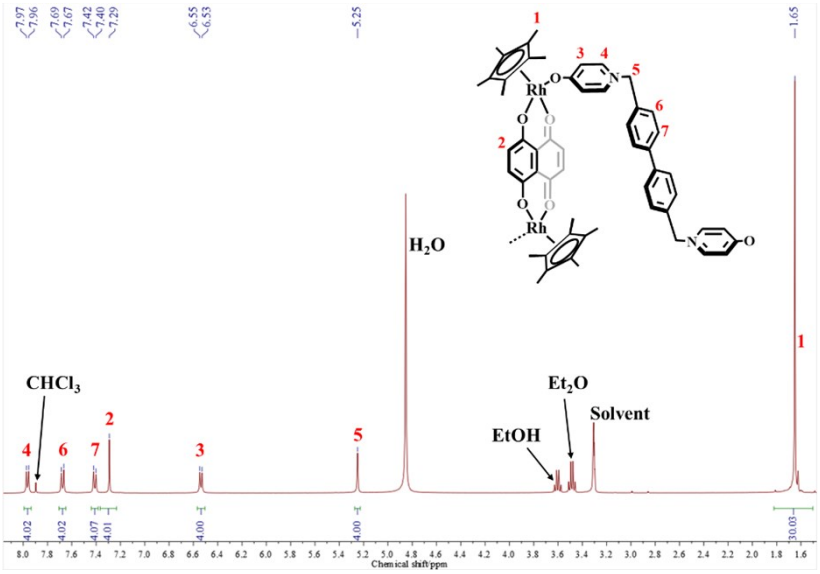

Fig.S15 ^{1}H NMR spectrum of 1D-chain **3**.

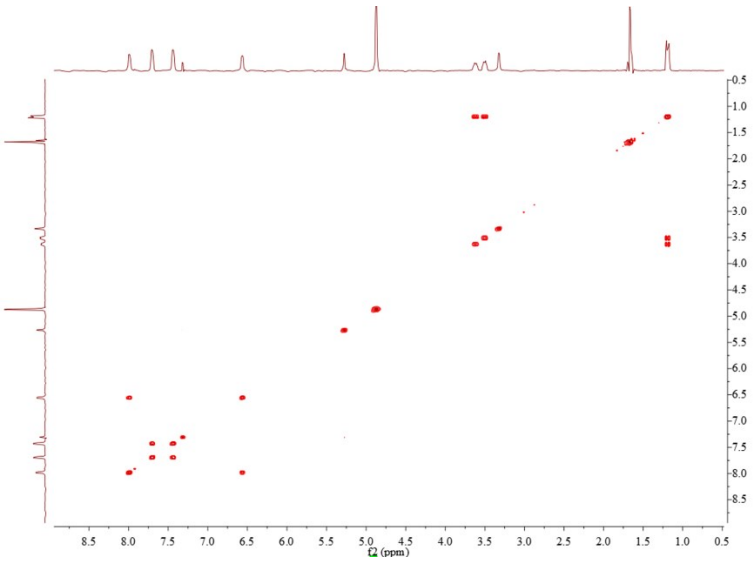

Fig.S16 ^{1}H-^{1}H COSY NMR spectrum of 1D-chain **3**.

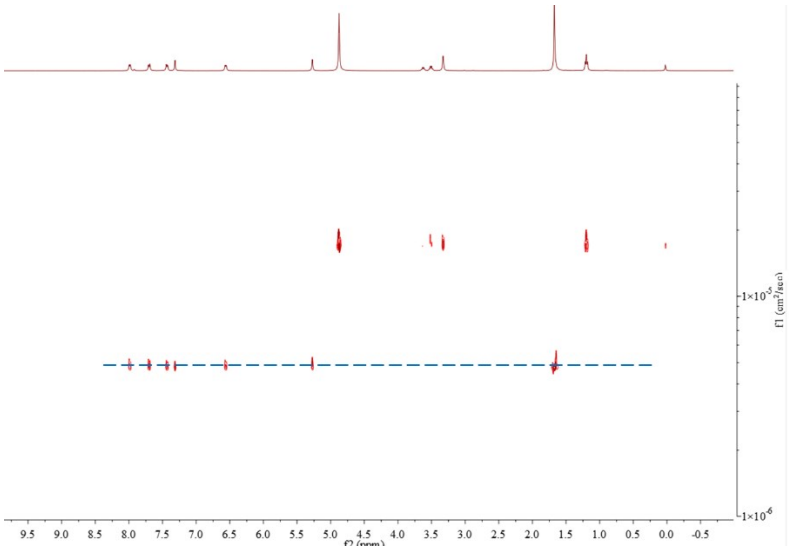

Fig.S17 ^{1}H DOSY NMR of 1D-chain **3**.

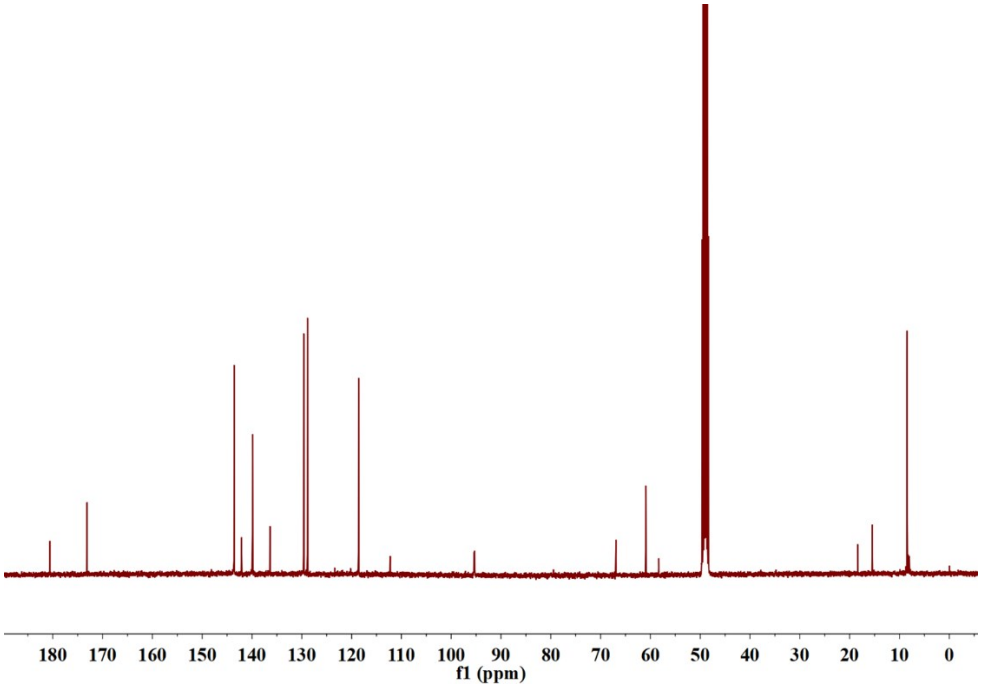

Fig.S18 ^{13}C spectrum of 1D-chain 3.

Crystal data and structure refinement for complexes

Table 1: Crystal data and structure refinement for trefoil knot 1.

Empirical formula	$C_{192}\ H_{240}\ F_{18}\ N_6\ O_{60}\ Rh_6\ S_6$	
Formula weight	4743.71	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 38.096(5) Å	α= 90°
	b = 42.405(5) Å	β= 111.252(7)°
	c = 15.0046(18) Å	γ = 90°
Volume	22591(5) $Å^3$	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	3.197 mm^{-1}	
F(000)	9768	
Crystal size	0.630 x 0.490 x 0.330 mm^3	
Theta range for data collection	2.927 to 54.497°	
Index ranges	-46<=h<=46, -51<=k<=51, -18<=l<=17	
Reflections collected	115518	
Independent reflections	21148 [R(int) = 0.1060]	
Completeness to theta = 53.594°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.339	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21148 / 218 / 1058	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2sigma(I)]	R1 = 0.1186, wR2 = 0.3531	
R indices (all data)	R1 = 0.1419, wR2 = 0.3828	
Extinction coefficient	0.000093(18)	
Largest diff. peak and hole	1.215 and -0.868 $e.Å^{-3}$	

Table 2: Crystal data and structure refinement for trefoil knot 2.

Empirical formula	$C_{194}\ H_{202}\ F_{18}\ N_6\ O_{48}\ Rh_6\ S_6$	
Formula weight	4537.42	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 38.3335(18) Å	α= 90°
	b = 42.1187(18) Å	β= 111.437(2)°
	c = 14.9706(7) Å	γ = 90°
Volume	22498.7(18) $Å^3$	
Z	4	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	3.170 mm^{-1}	
F(000)	9280	
Crystal size	0.530 x 0.220 x 0.120 mm^3	
Theta range for data collection	2.943 to 54.989°.	
Index ranges	-46<=h<=46, -51<=k<=51, -18<=l<=16	
Reflections collected	139566	
Independent reflections	21379 [R(int) = 0.1052]	
Completeness to theta = 53.594°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.482	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21379 / 242 / 1056	
Goodness-of-fit on F^2	1.125	
Final R indices [I>2sigma(I)]	R1 = 0.1263, wR2 = 0.3739	
R indices (all data)	R1 = 0.1513, wR2 = 0.3995	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.130 and -1.479 $e.Å^{-3}$	

Table 3: Crystal data and structure refinement for one-dimension chain 3.

Empirical formula	C_{60} H_{72} F_6 N_2 O_{17} Rh_2 S_2	
Formula weight	1477.13	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.3272(13) Å	α= 90°
	b = 25.9944(13) Å	β= 121.863(2)°
	c = 15.3921(7) Å	γ = 90°
Volume	7927.0(7) $Å^3$	
Z	4	
Density (calculated)	1.238 Mg/m^3	
Absorption coefficient	2.996 mm^{-1}	
F(000)	3032	
Crystal size	0.550 x 0.130 x 0.080 mm^3	
Theta range for data collection	2.929 to 54.498°.	
Index ranges	-28<=h<=28, -31<=k<=31, -15<=l<=18	
Reflections collected	25891	
Independent reflections	7406 [R(int) = 0.0764]	
Completeness to theta = 53.594°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.358	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7406 / 92 / 365	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0904, wR2 = 0.2513	
R indices (all data)	R1 = 0.0990, wR2 = 0.2646	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.053 and -1.308 e.$Å^{-3}$	

Table 4: Crystal data and structure refinement for one-dimension chain 4.

Empirical formula	$C_{62}\ H_{59}\ F_6\ N_3\ O_{12}\ Rh_2\ S_2$	
Formula weight	1422.06	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.466(3) Å	α= 90°
	b = 8.3663(8) Å	β= 95.104(4)°
	c = 25.342(2) Å	γ = 90°
Volume	6222.6(10) $Å^3$	
Z	4	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	3.718 mm^{-1}	
F(000)	2896.0	
Crystal size	0.510 x 0.190 x 0.080 mm^3	
Theta range for data collection	3.838 to 56.988°	
Index ranges	$-36 \leq h \leq 36, -10 \leq k \leq 10, -31 \leq l \leq 28$	
Reflections collected	24535	
Independent reflections	6369 [R_{int} = 0.0973, R_{sigma} = 0.0681]	
Completeness to theta = 53.594°	100 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.519	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6369 / 0 /384	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1110	
R indices (all data)	R1 = 0.0670, wR2 = 0.1216	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.88 and -0.54 e $Å^{-3}$	