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ARTICLES

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# A synthetic molecular pentafoil knot

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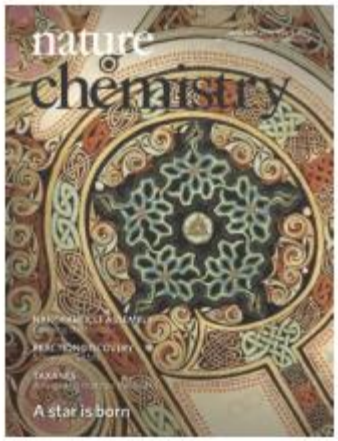
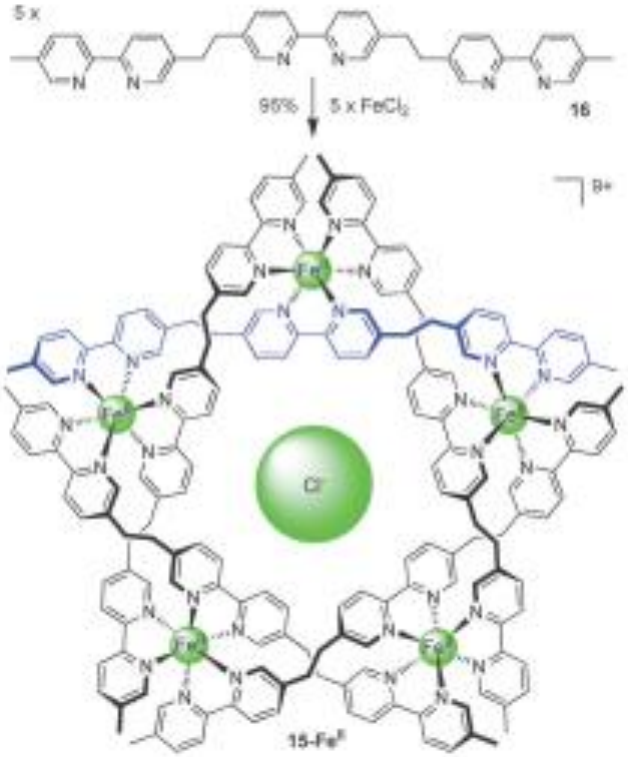
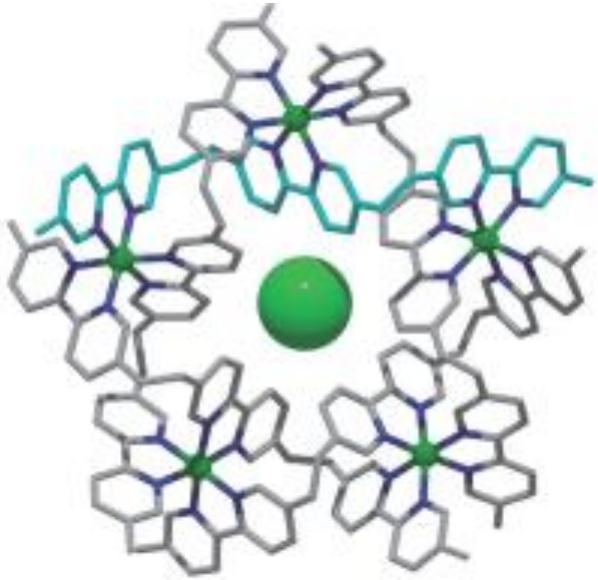


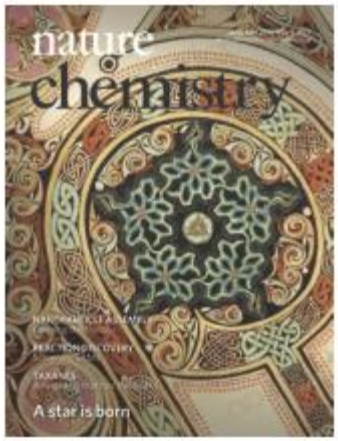

## COVER IMAGE

The cover image features the interlaced 'rho' character from Matthew 1:18 in the Lindisfarne Gospels as a backdrop for the X-ray crystal structure of the most complex non-DNA molecular knot synthesized so far. A team led by David Leigh prepared the 160-atom-long pentafoil knot in a one-step reaction from ten organic building blocks and five iron(II) cations. They use a single chloride anion as a template, which, in the solid-state structure, is located at the centre of the pentafoil knot and exhibits ten **CH···Cl**$^-$ hydrogen bonds.

Article p15; News & Views p7



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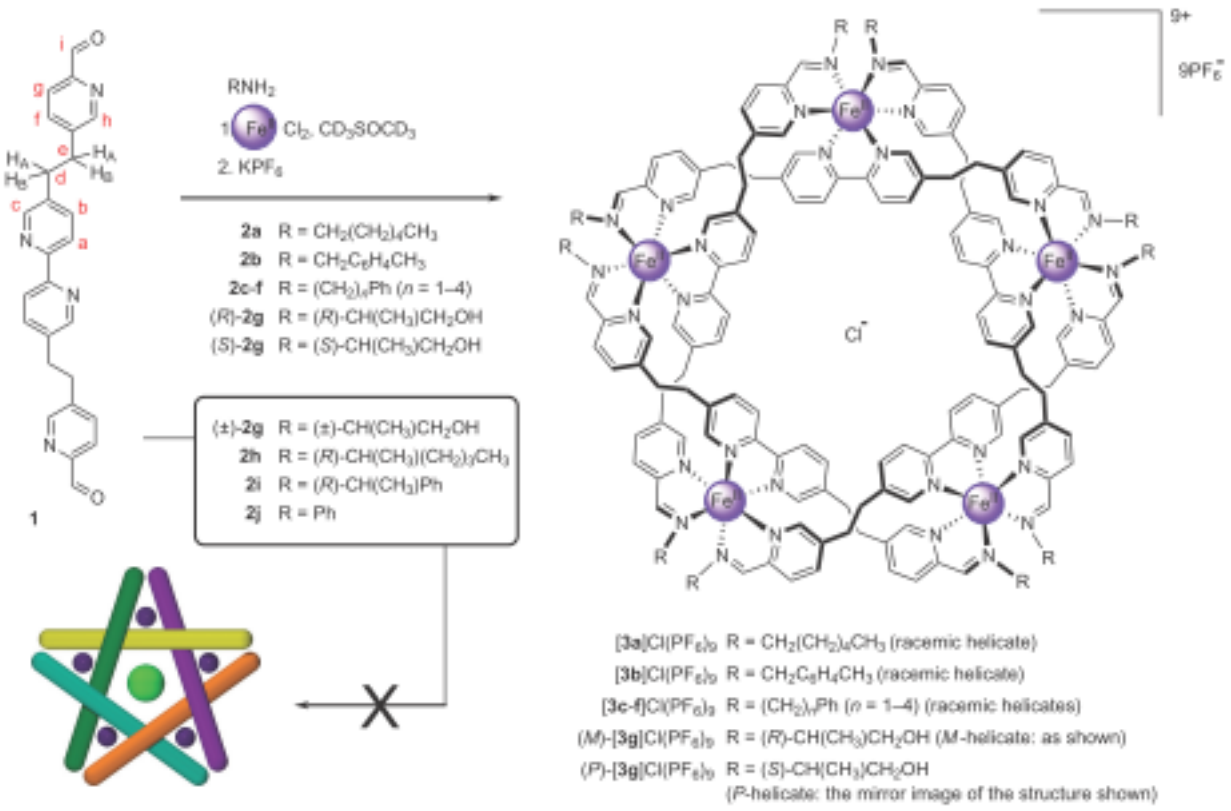
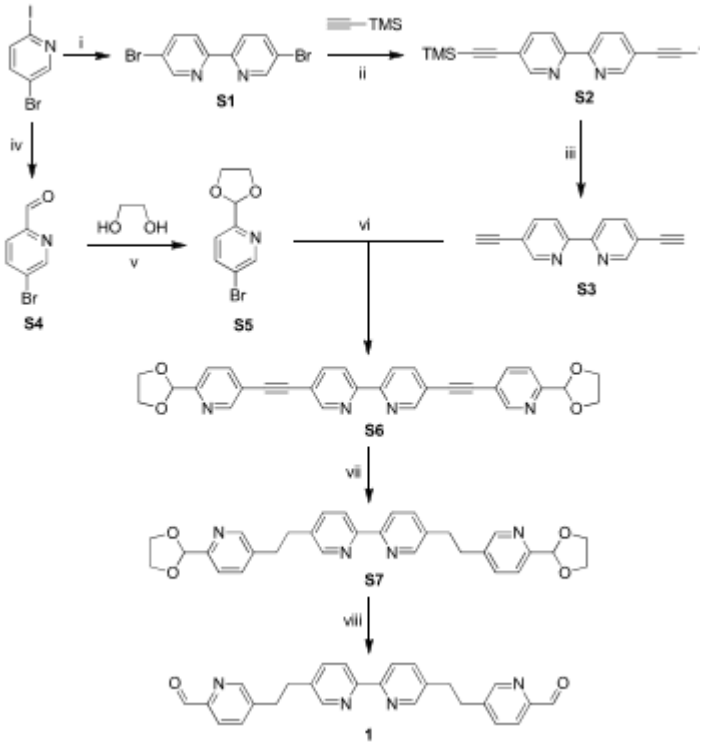
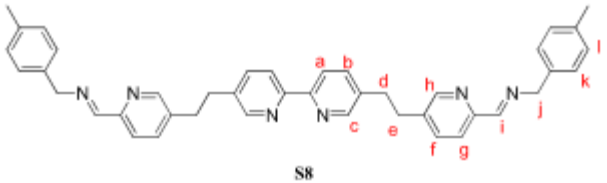
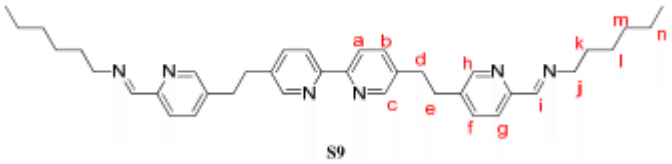
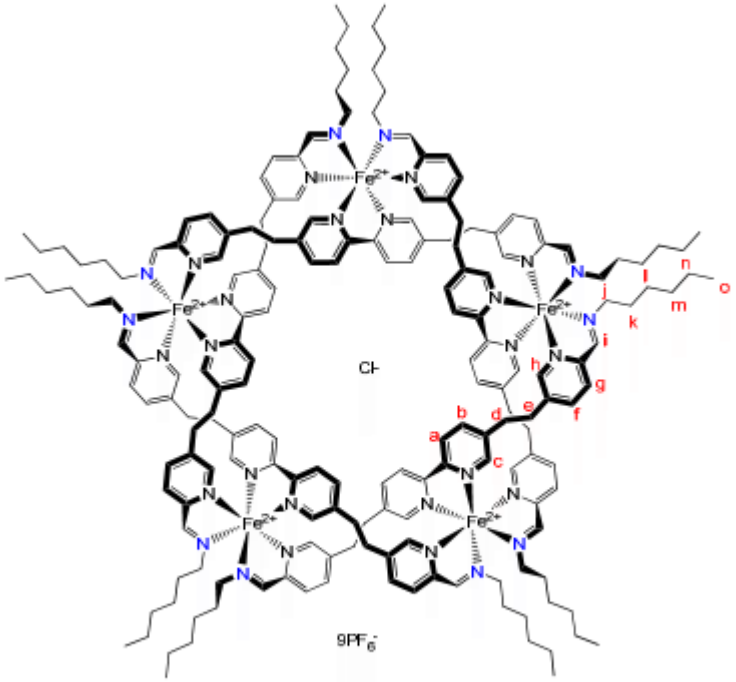


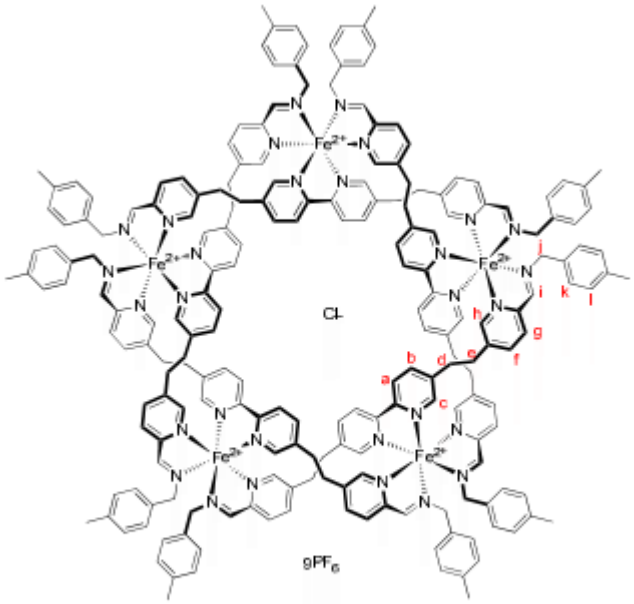

i
ii
iii
iv
v
vi
vii
viii
TMS
S1
S2
S3
S4
S5
S6
S7
1


S8


S9




[**3a**]Cl($PF_6$)$_9$




[**3b**]Cl($PF_6$)$_9$

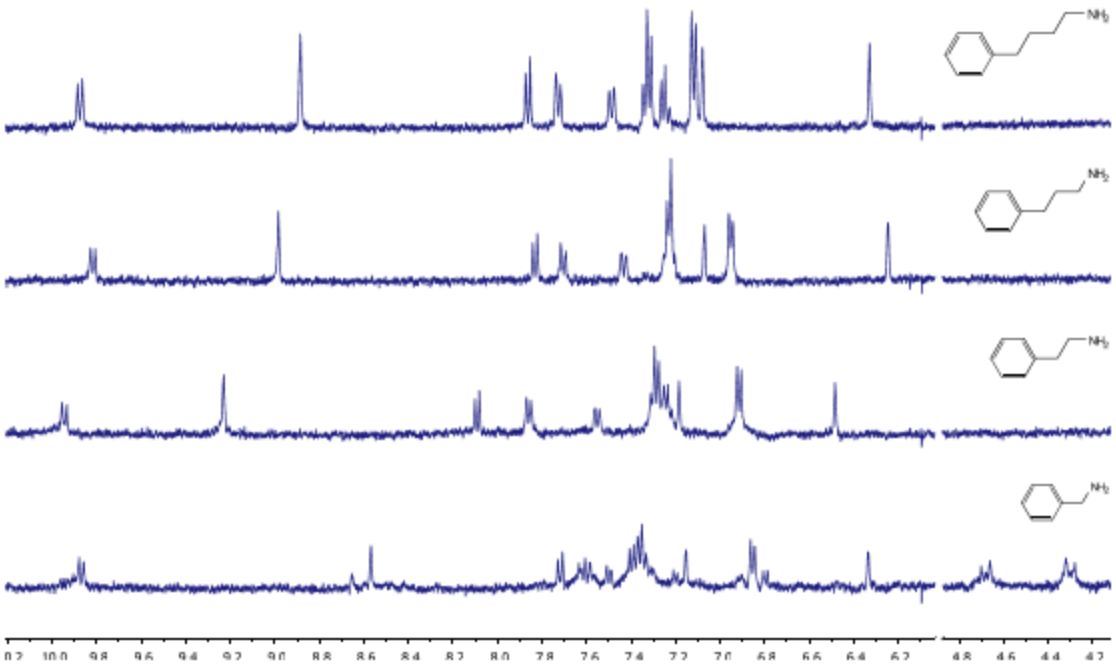
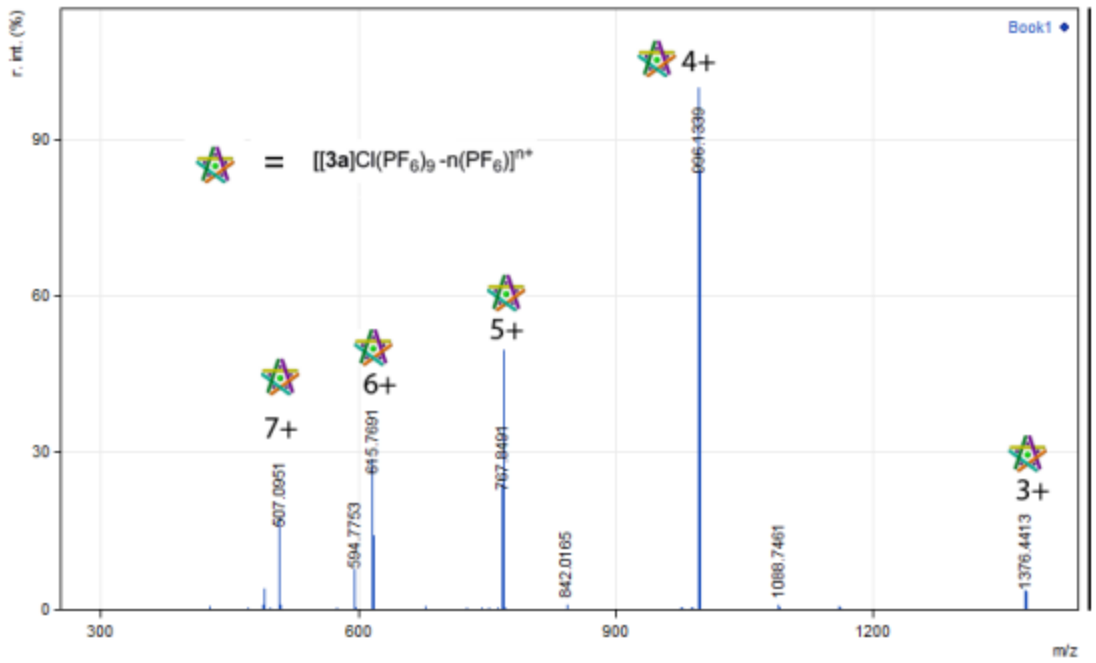
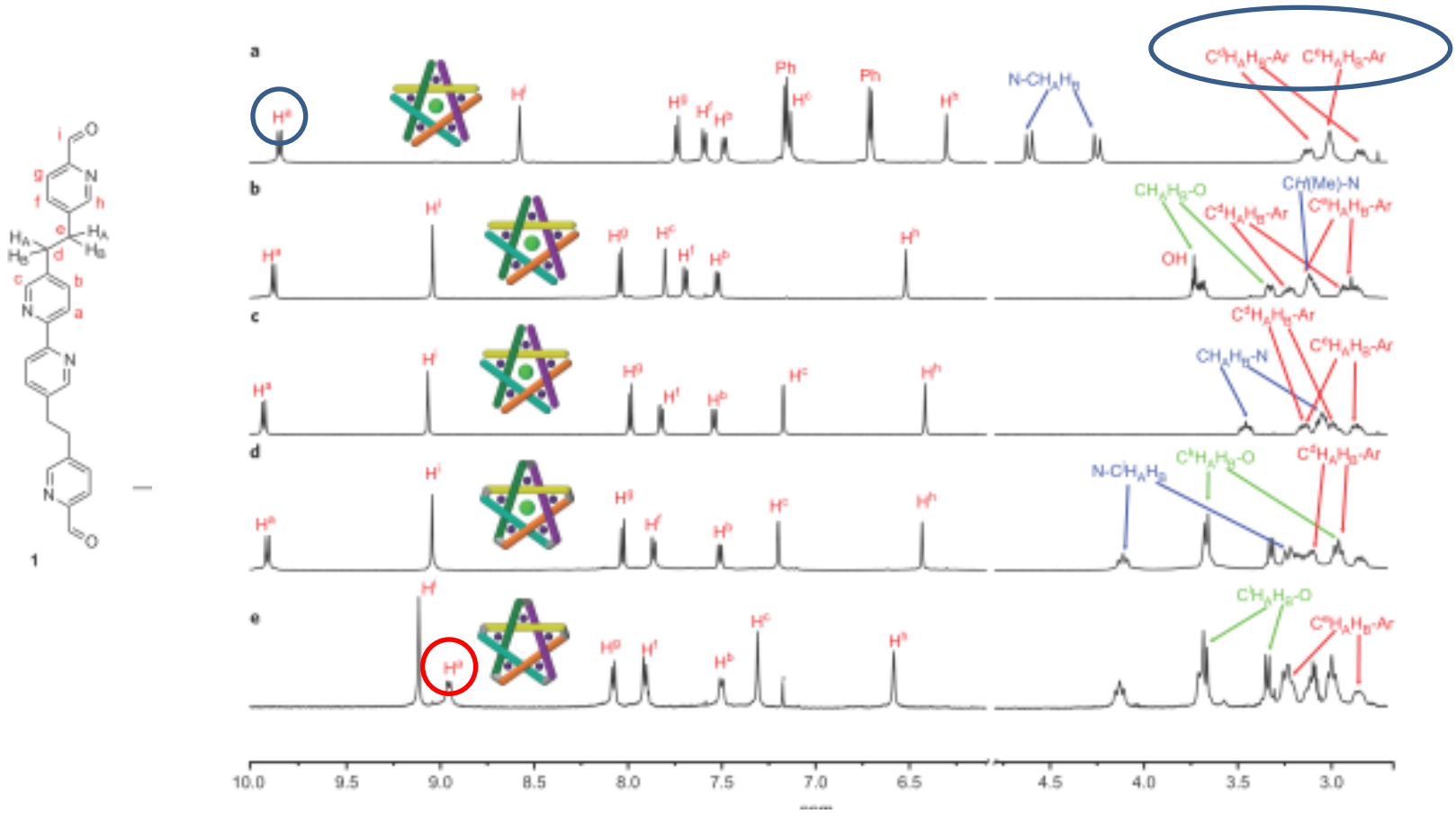


**Figure S3** $^{1}$H NMR ($CD_3CN$, 500 MHz) of helicates **3c-f**.


Book1
r. int. (%)
90
60
30
0
300
600
900
1200
m/z
= [[3a]Cl(PF6)9 -n(PF6)]n+
4+
5+
6+
7+
3+
996.1339
767.8491
615.7691
607.0951
594.7753
842.0165
1088.7461
1376.4413


a
b
c
d
e
Ph
Ph
N-CHAHB
C6HAHB-Ar
C6HAHB-Ar
CH2HB-O
CH(Me)-N
C4HAHB-Ar
C6HAHB-Ar
OH
C4HAHB-Ar
C6HAHB-Ar
CH2HB-N
N-CHAHB
C5HAHB-O
C4HAHB-Ar
C5HAHB-O
C6HAHB-Ar
10.0
9.5
9.0
8.5
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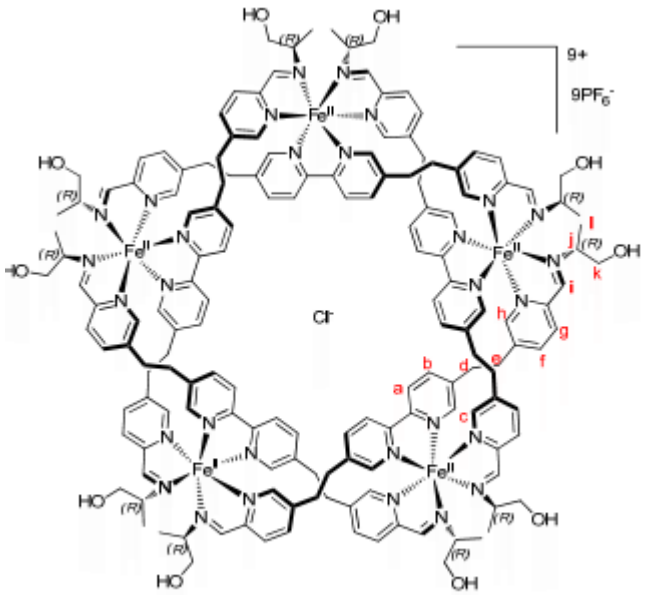
7.5
7.0
6.5
4.5
4.0
3.5
3.0

1




*M*-(ΔΔΔΔΔ)-[3g]Cl(PF$_6$)$_9$

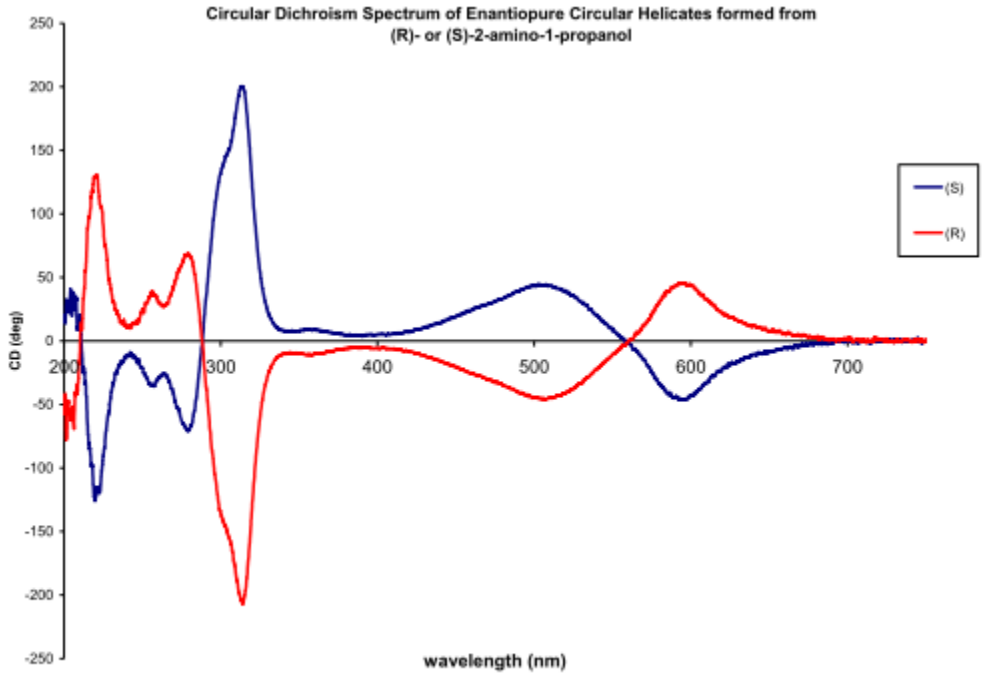
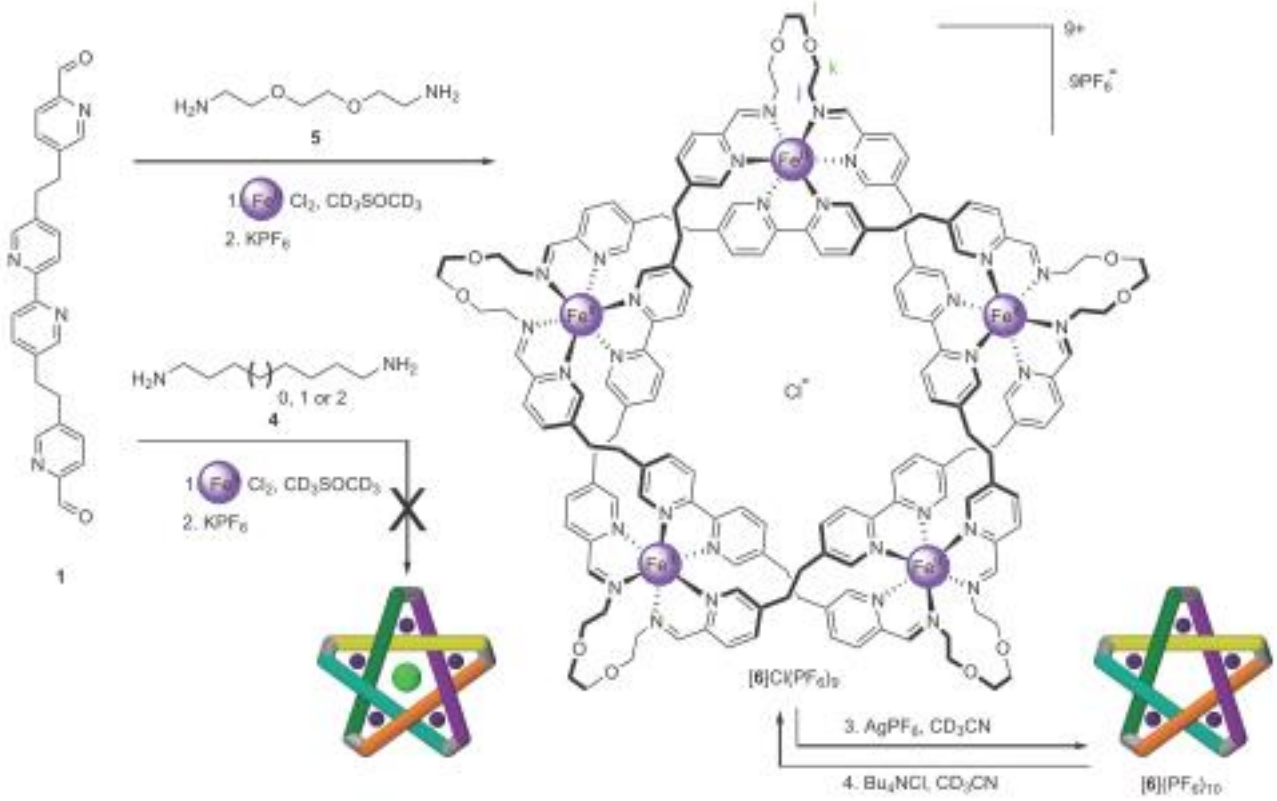



**Figure S8** Circular dichroism spectra of (*R*)-[**3g**]Cl$(PF_6)_9$ and (*S*)-[**3g**]Cl$(PF_6)_9$ in MeCN.


1
5
1. Fe2+ Cl2, CD3SOCD3
2. KPF6
4
0, 1 or 2
1. Fe2+ Cl2, CD3SOCD3
2. KPF6
9+
9PF6-
Cl-
[6]Cl(PF6)9
3. AgPF6, CD3CN
4. Bu4NCl, CD3CN
[6](PF6)10

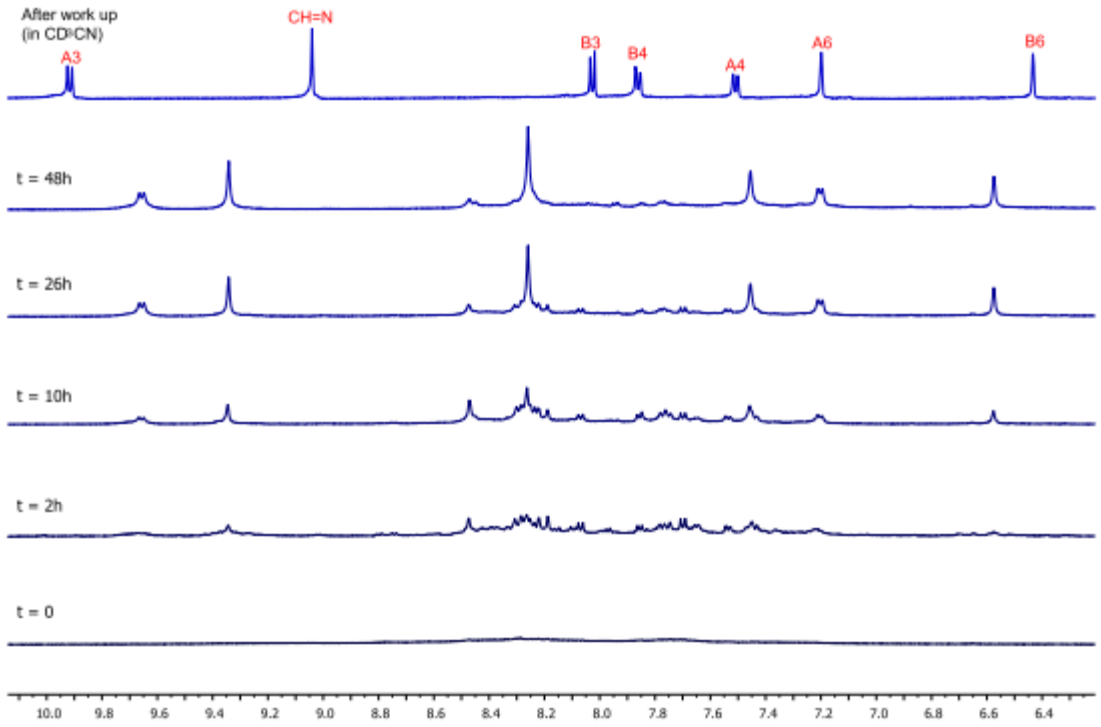
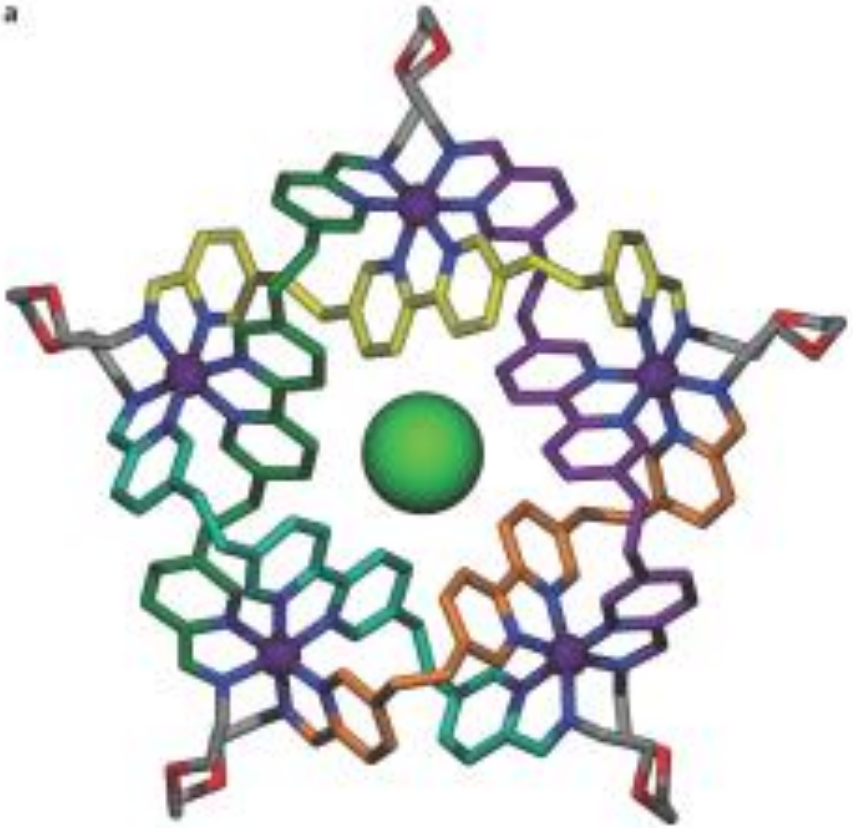
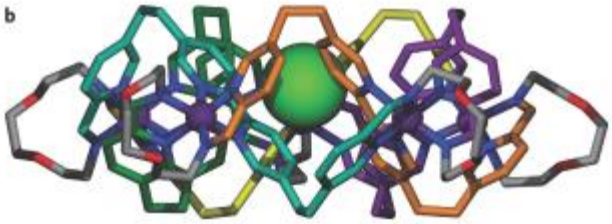


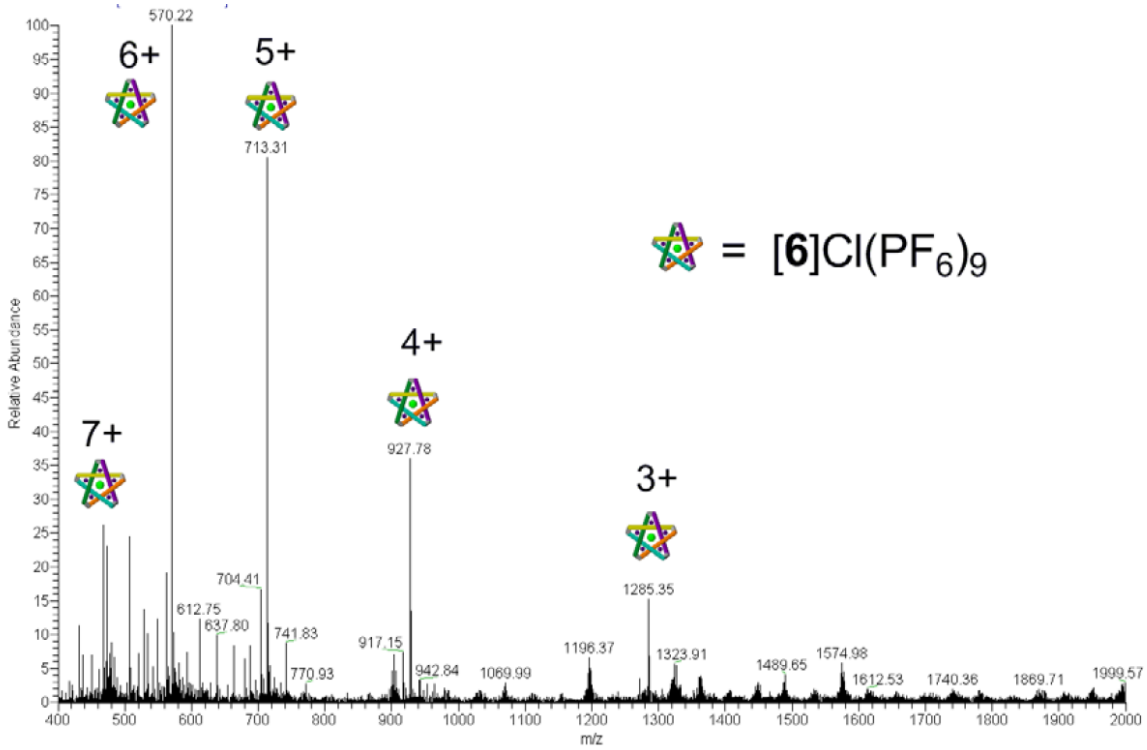

**Figure S9** Formation of pentafoil knot $[\mathbf{6}]^{10+}$ monitored by $^1$H NMR (DMSO-$d_6$, 500 MHz), aromatic region of spectrum shown. Spectra were collected of the crude reaction mixture after t = 0 (bottom), 2h, 10h, 26h and 48h. The top spectra is of the same sample after work-up ($^1$H NMR in $CD_3CN$) with $^1$H NMR assignments indicated.

a



b





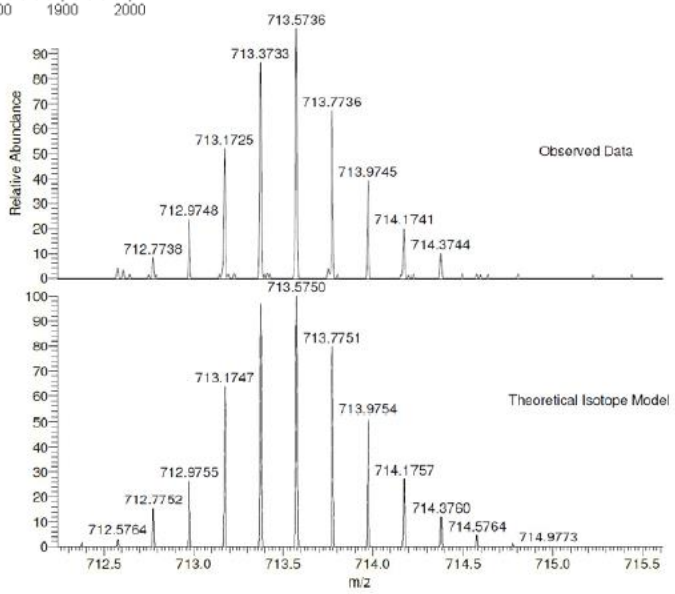
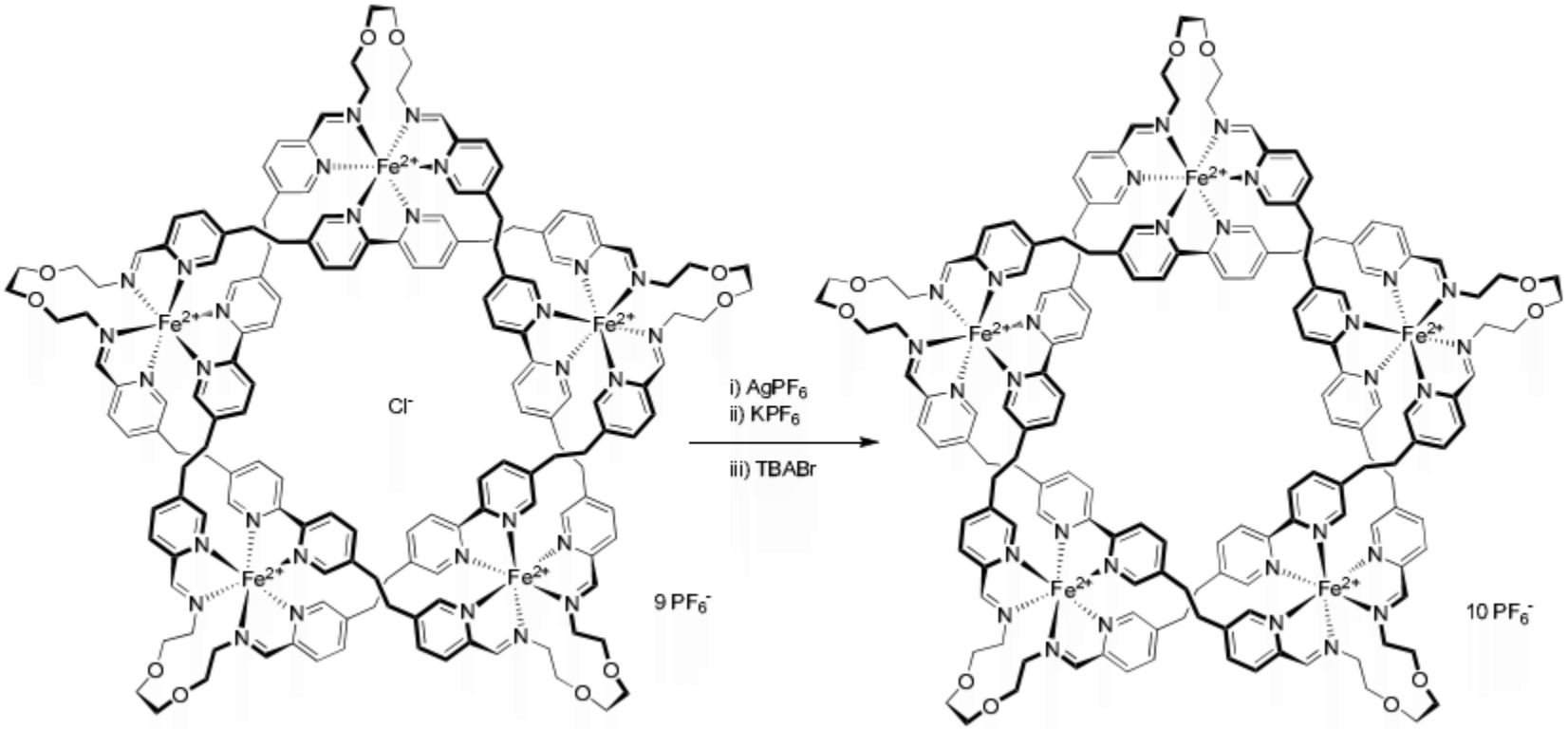
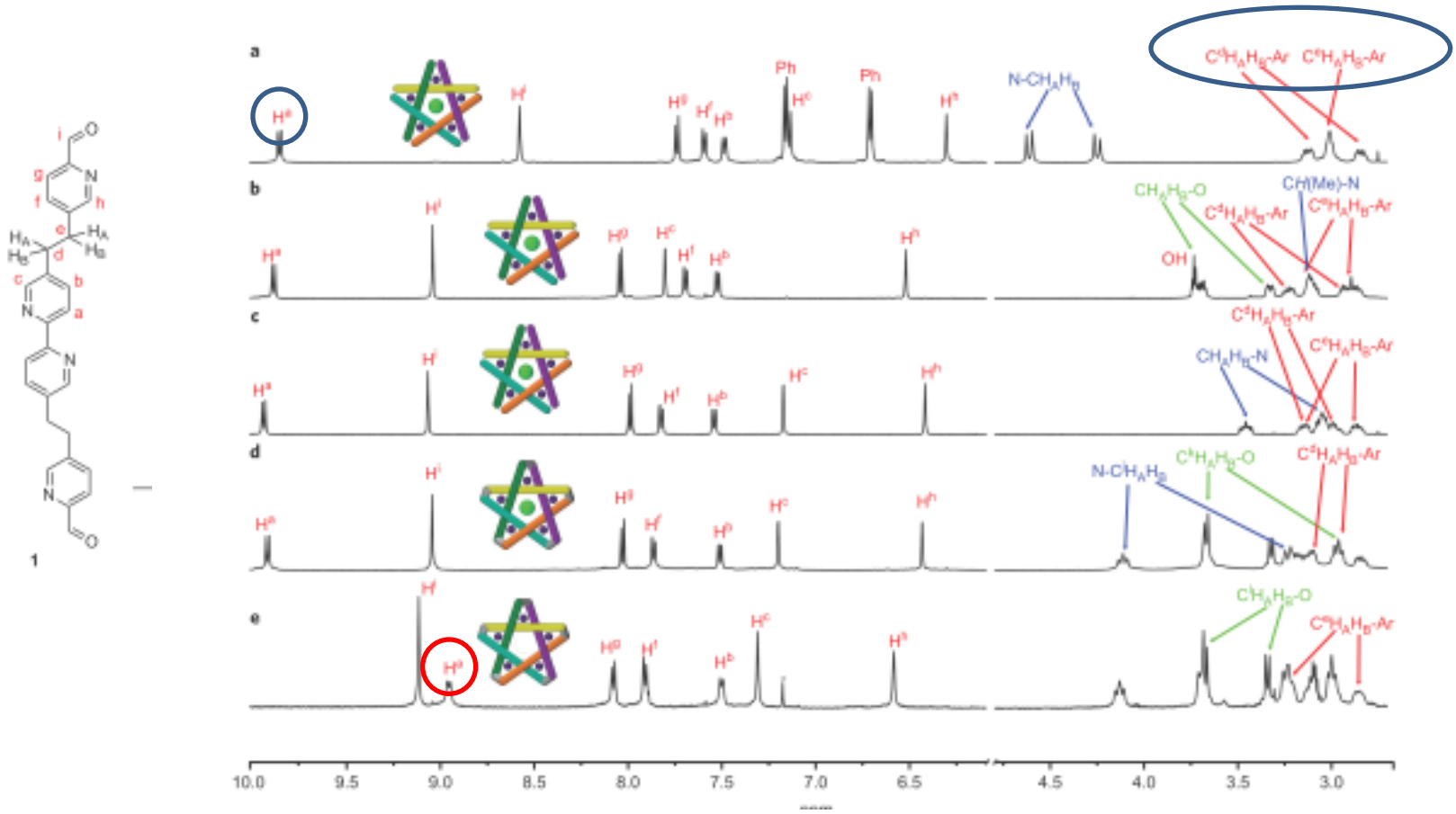




**Figure S5** Low-resolution ESI-MS of pentafoil knot [**6**]$Cl(PF_6)_9$ (top), and high-resolution isotope pattern (bottom) of $[M\text{-}4PF_6]^{5+}$ peak.


Cl-
9 PF6-
i) AgPF6
ii) KPF6
iii) TBABr
10 PF6-


a
b
c
d
e
Ph
Ph
N-CHAHB
C6HAHB-Ar
C6HAHB-Ar
CH2HB-O
CH(Me)-N
C4HAHB-Ar
C6HAHB-Ar
OH
C4HAHB-Ar
C6HAHB-Ar
CH2HB-N
N-CHAHB
C5HAHB-O
C4HAHB-Ar
C5HAHB-O
C6HAHB-Ar
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
4.5
4.0
3.5
3.0

1