Supplementary Information

Site-Selective Anion Recognition of an Interlocked Dimer

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Table S1. Crystallographic parameters of **3**.

Compound	[**3**+$(NO_3)_8$] [a]	[**3**+$(NO_3)_8$] [a]
Vapor	2-propanol	1,4-dioxane
Formula	$C_{200}H_{152}N_{16}O_{40}Pd_4$	$C_{200}H_{160}N_{16}O_{40}Pd_4$
Formula weight	3845.17	3853.03
Crystal system	Tetragonal	Tetragonal
Space group	*P*4/*nnc* (#126)	*P*4/*nnc* (#126)
a/ Å	18.9341(8)	18.9525(12)
b/ Å	18.9341(8)	18.9525(12)
c/ Å	38.159(3)	38.292(4)
α/ º	90	90
β/ º	90	90
γ/ º	90	90
V/ Å^3	13679.9(17)	13754(2)
$d_{calc.}$ /g cm^{-3}	0.93	0.93
Z	2	2
$2\theta_{max}$/º	49.5	41.7
μ (MoKα) /mm^{-1}	0.314	0.312
Temperature /K	103	123
Crystal form	block	block
Crystal size /mm^3	0.12 × 0.11 × 0.08	0.10 × 0.08 × 0.06
Crystal color	colorless	colorless
# of total reflections	65225	45364
# of unique reflections	5869	3643
# of observed reflections	3416	2030
R_{int}	0.058	0.060
Criterion for observed reflections	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$
$R1(F_o)$	0.074	0.099
$wR2(F_o^2)$	0.202	0.284
G. O. F.	1.000	1.092
# of parameters used	306	230
$\Delta\rho_{max}$ (eÅ^{-3})	+1.349	+1.138
$\Delta\rho_{min}$ (eÅ^{-3})	−0.501	−0.441
CCDC number	1405236	1405237

[a] Formula, formula weight, density, and absorption coefficient are known contents only.

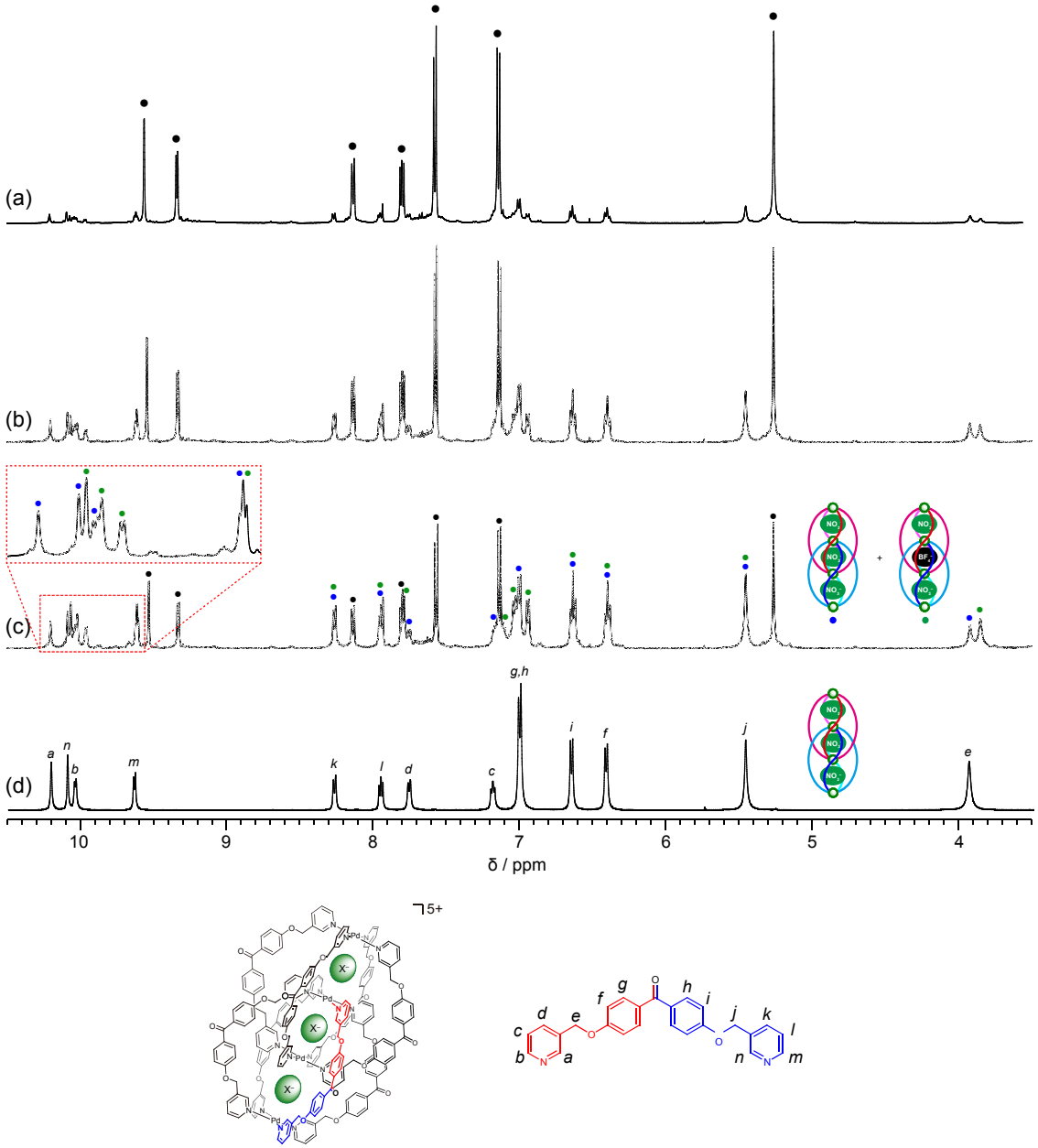

Figure S1. ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of the solution of [**1**+$(BF_4)_4$] (5.0 mM) + $TBANO_3$ (5.0 mM) after heating of (a) 12 h, (b) 62 h, and (c) 154 h (equilibrium state). (d) ^{1}H NMR spectrum (500 MHz, DMSO-d_6, rt) of ***F***. Black, green, and blue filled circles denote monomer **1**, ***C***, and ***F***, respectively.

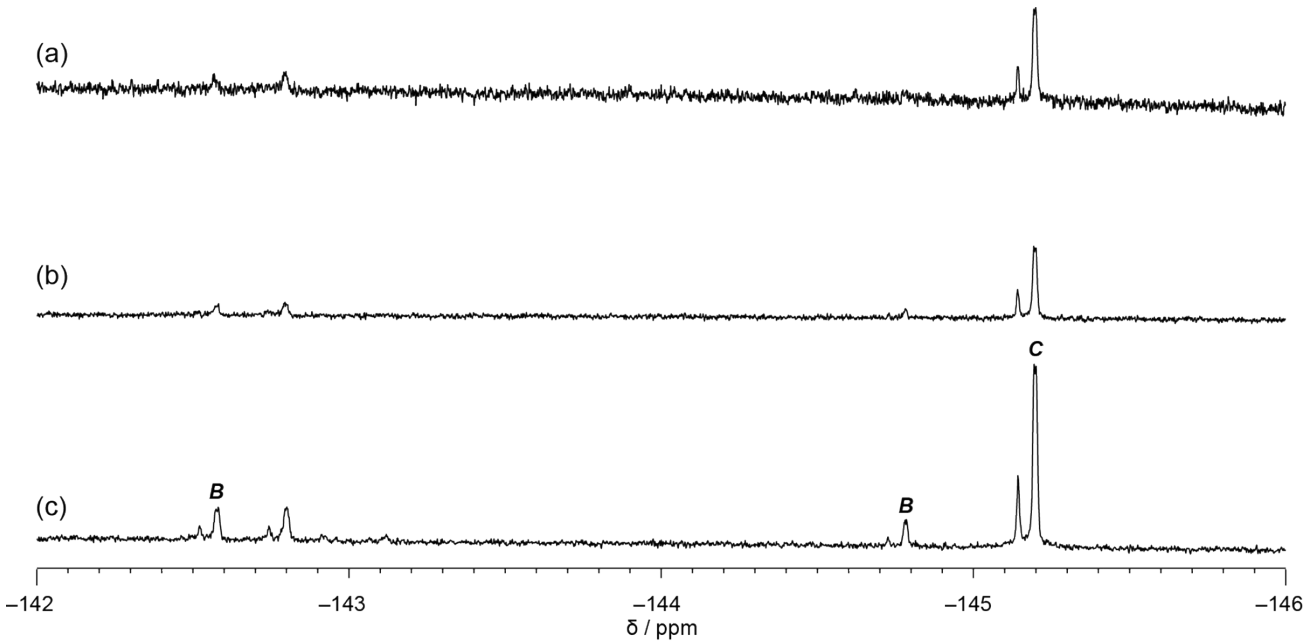

Figure S2. ^{19}F NMR spectra (500 MHz, DMSO-d_6, rt) of the solution of [**1**+$(BF_4)_4$] (5.0 mM) + $TBANO_3$ (5.0 mM) after heating of (a) 12 h, (b) 62 h, and (c) 154 h (equilibrium state).

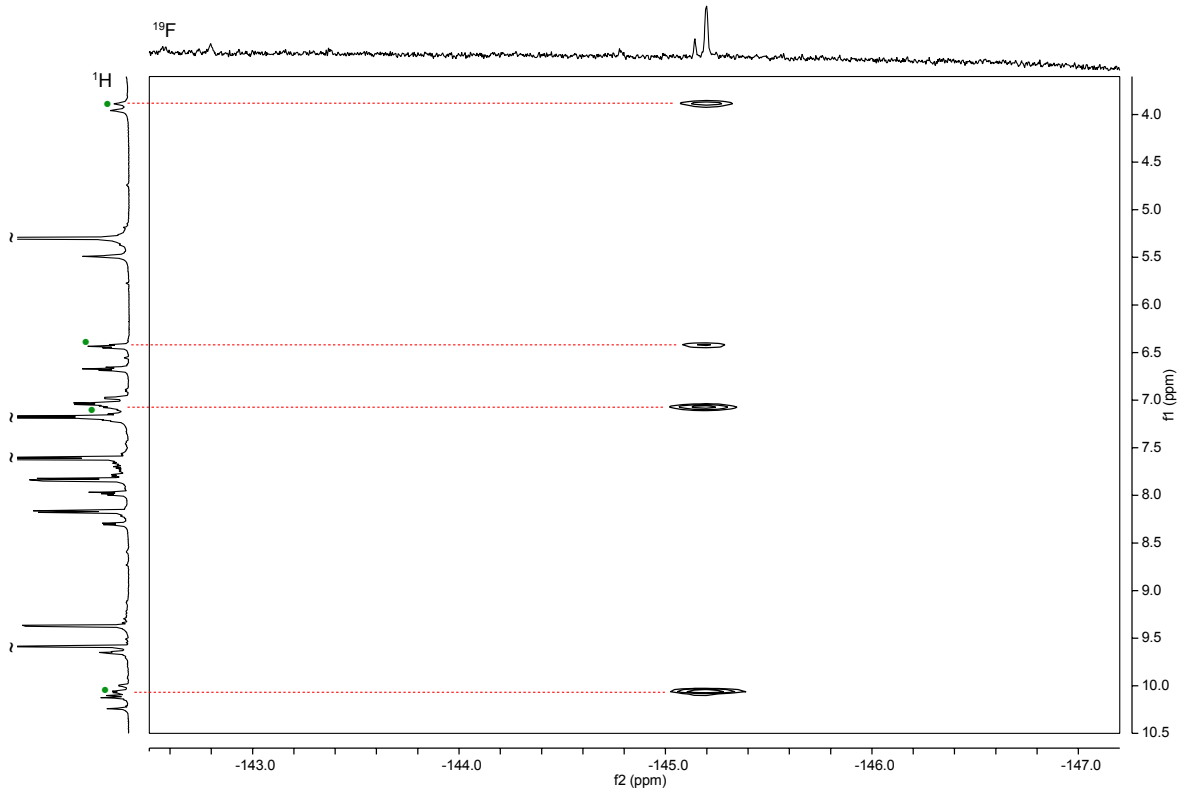

Figure S3. ^{19}F-^{1}H HOESY spectrum (470 MHz (^{19}F, f2), 500 MHz (^{1}H, f1), DMSO-d_6, rt) of the solution containing **1**, ***C***, and ***F***. Mixing time = 1.0 sec.

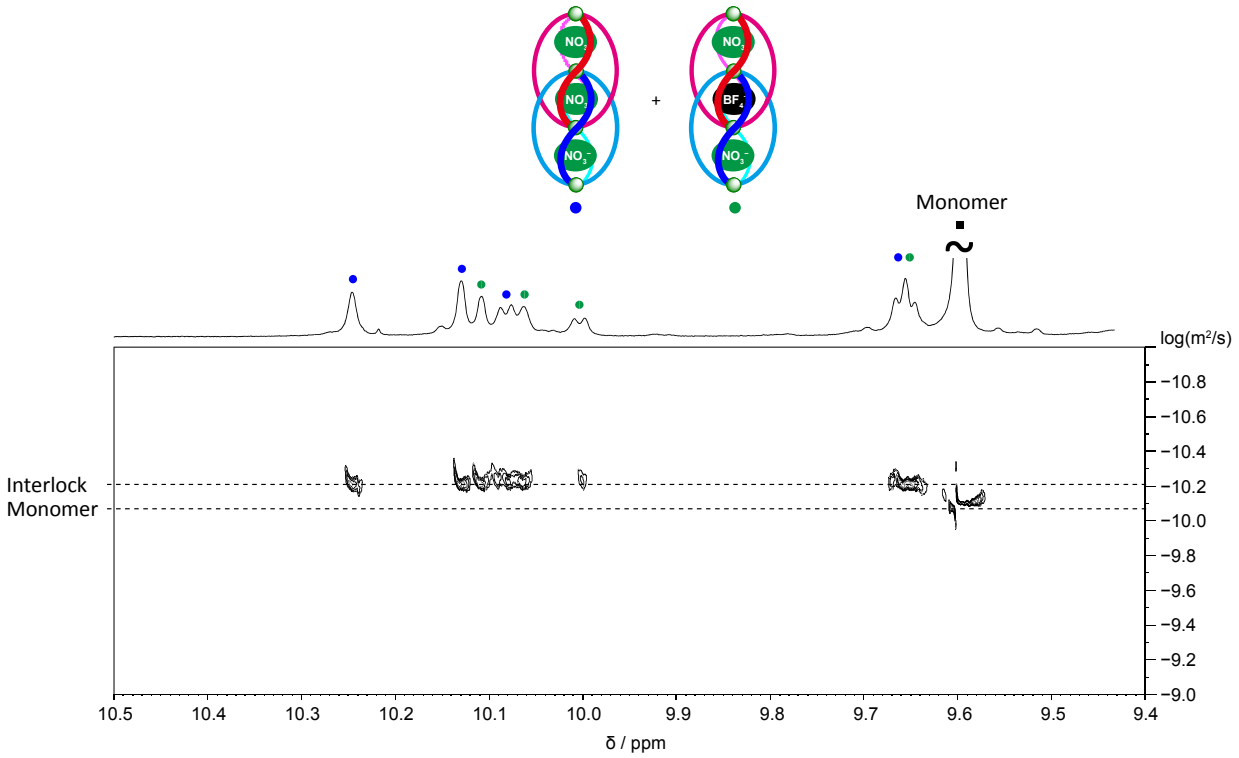

Figure S4. ^{1}H DOSY spectrum (500 MHz, DMSO-d_6, rt) of the solution containing of **1**, ***C***, and ***F***.

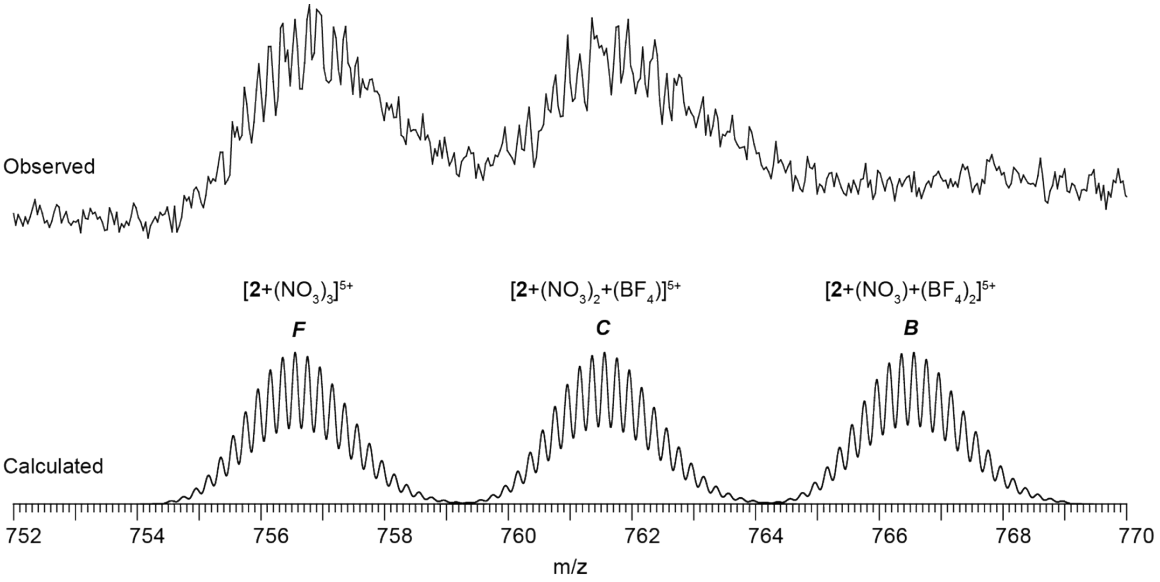

Figure S5. ESI MS spectrum of a mixture of **1**, ***C*** and ***F*** in DMSO-d_6. Top: observed ESI MS spectrum. Bottom: Calculated isotope patterns of [**2**+$(NO_3)_3$]$^{5+}$ (**F**), [**2**+$(NO_3)_2$+(BF_4)]$^{5+}$ (***C***), and [**2**+(NO_3)+$(BF_4)_2$]$^{5+}$ (***B***).

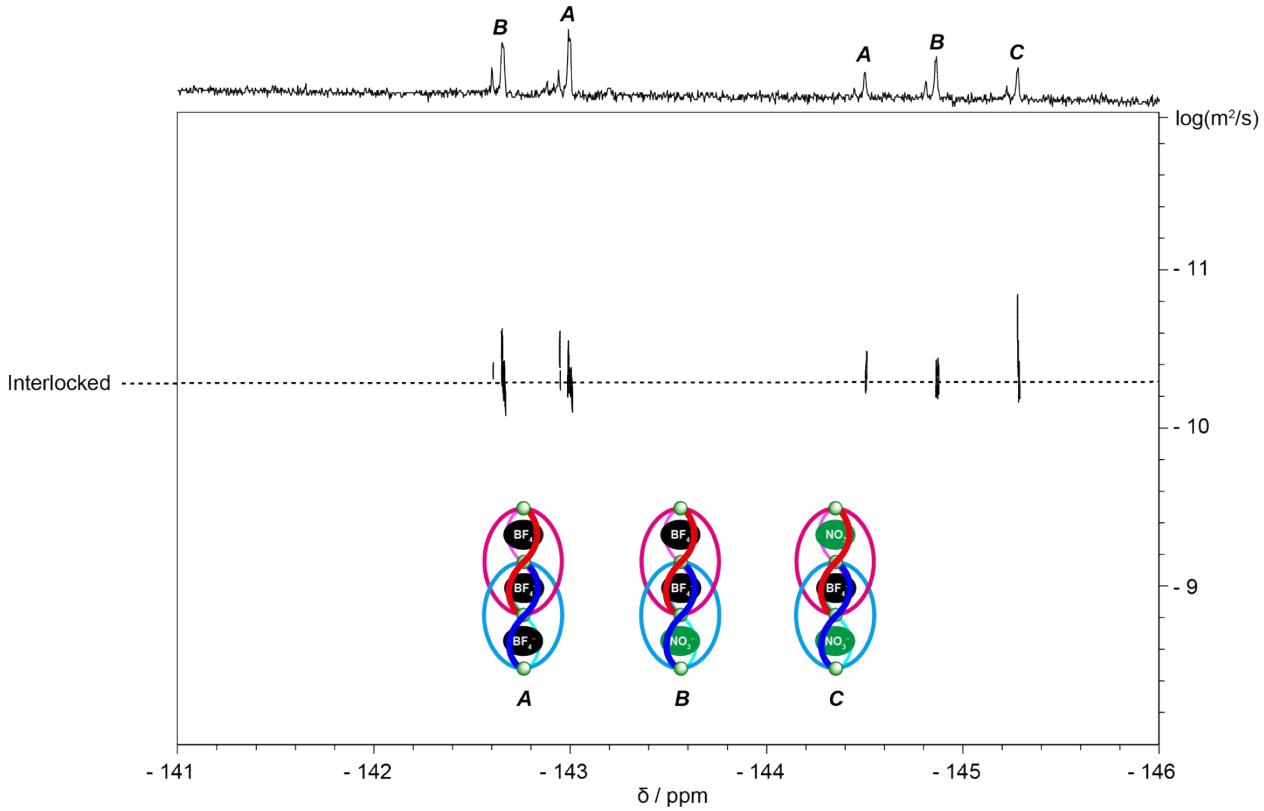

Figure S6. ^{19}F DOSY spectrum (500 MHz, DMSO-d_6, rt) of the solution containing ***A***, ***B*** and ***C***.

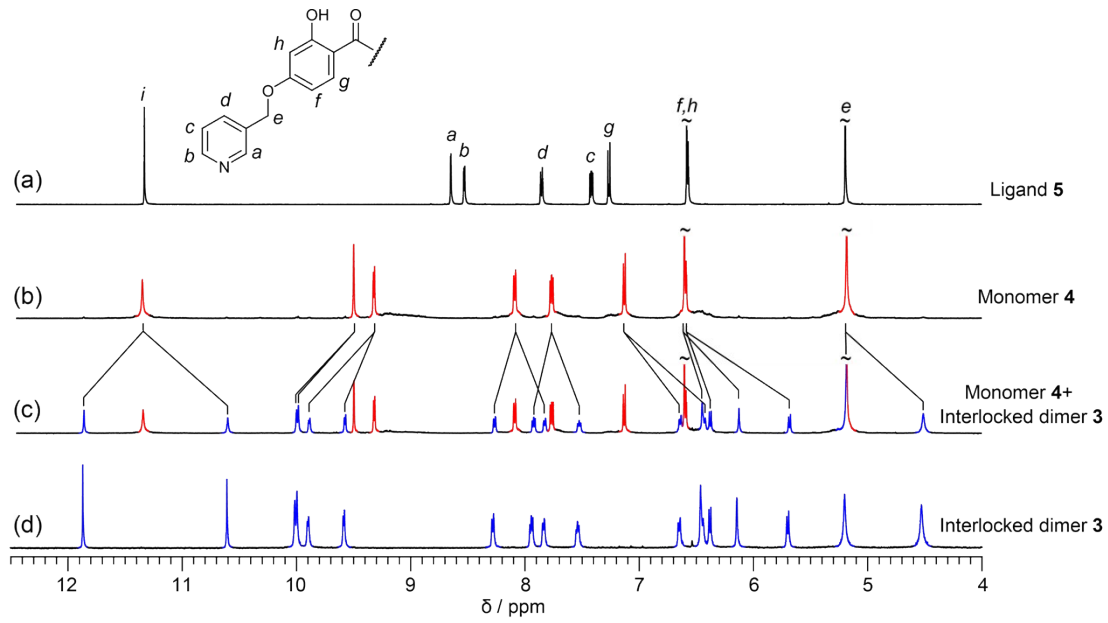

Figure S7. ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of (a) **5**, (b) **4** prepared by the reaction of $Pd(NO_3)_2$ with two equiv. of **5**, and (c) a mixture of **3** and **4**, and (d) **3**.

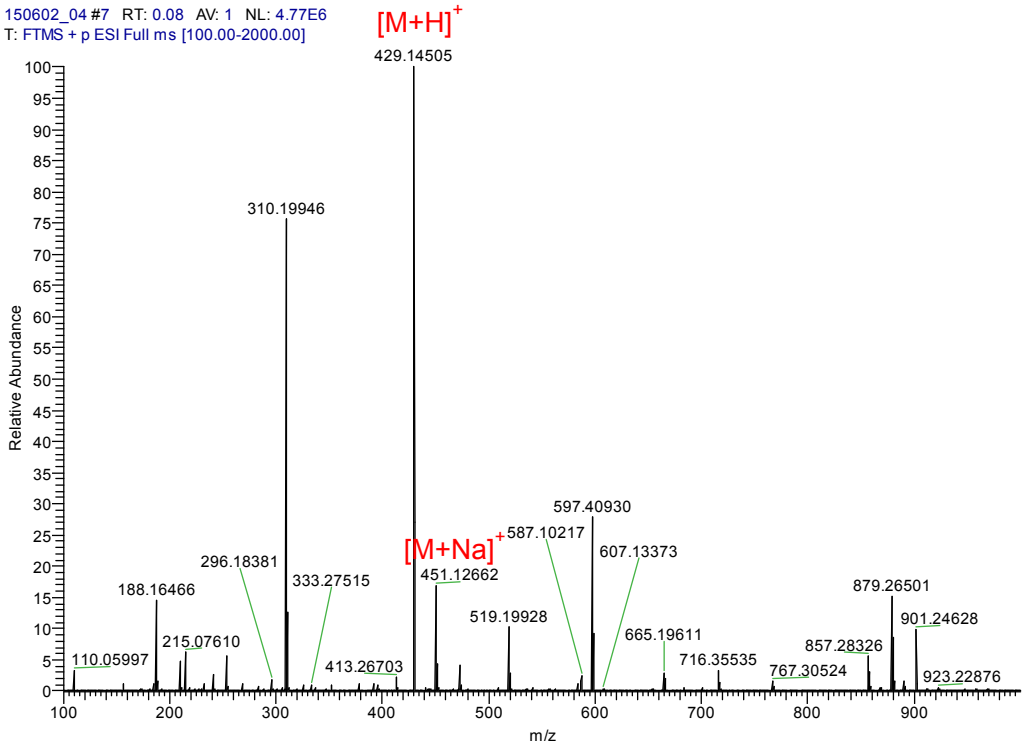

Figure S8. ESI-MS spectrum of **5** in MeOH. The spectrum was acquired on a Thermo Fisher Scientific LTQ Orbitrap XL.

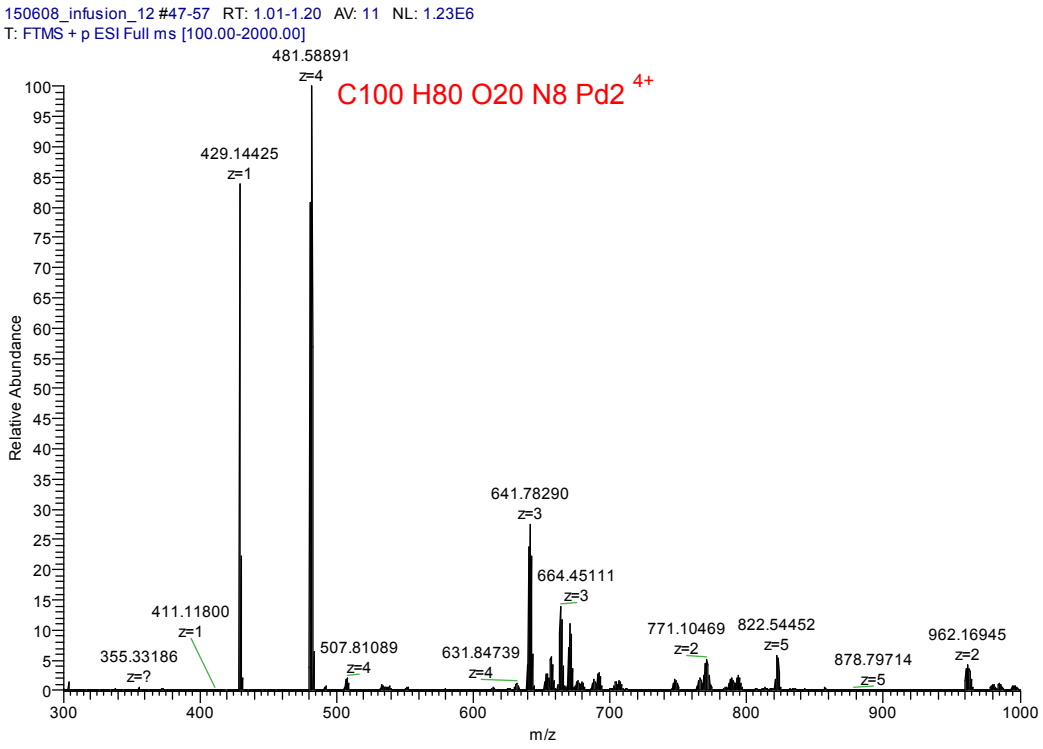

Figure S9. ESI-MS spectrum of the BF_4^- salt of **4** in DMSO. The spectrum was acquired on a Thermo Fisher Scientific LTQ Orbitrap XL.

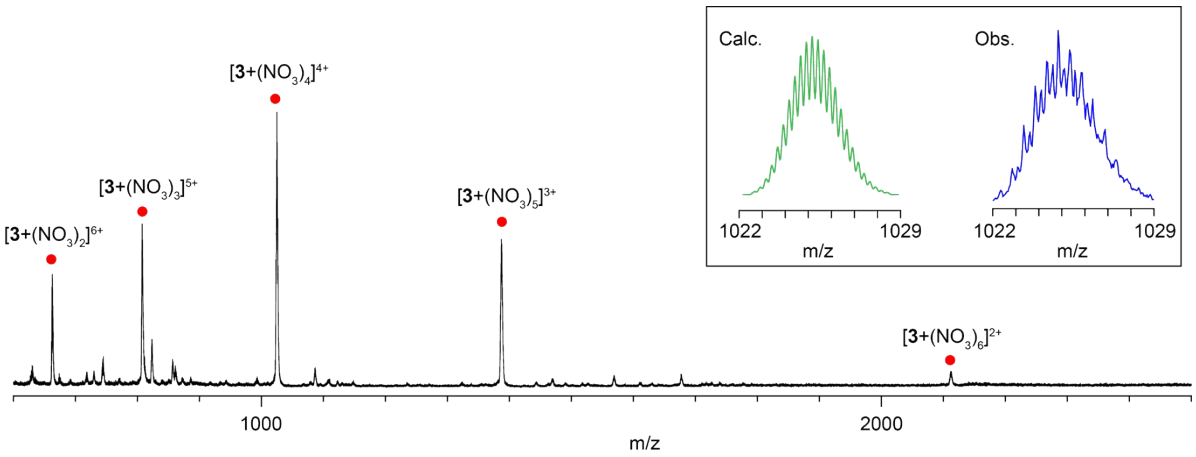

Figure S10. ESI-MS spectrum of **3** in the DMSO-d_6 solution. Inset: calculated (green) and observed (blue) isotope patterns of [**3**+$(NO_3)_5$]$^{3+}$. The spectrum was acquired on a Mariner^{TM} ESI-TOF MS Biospectrometry Workstation.

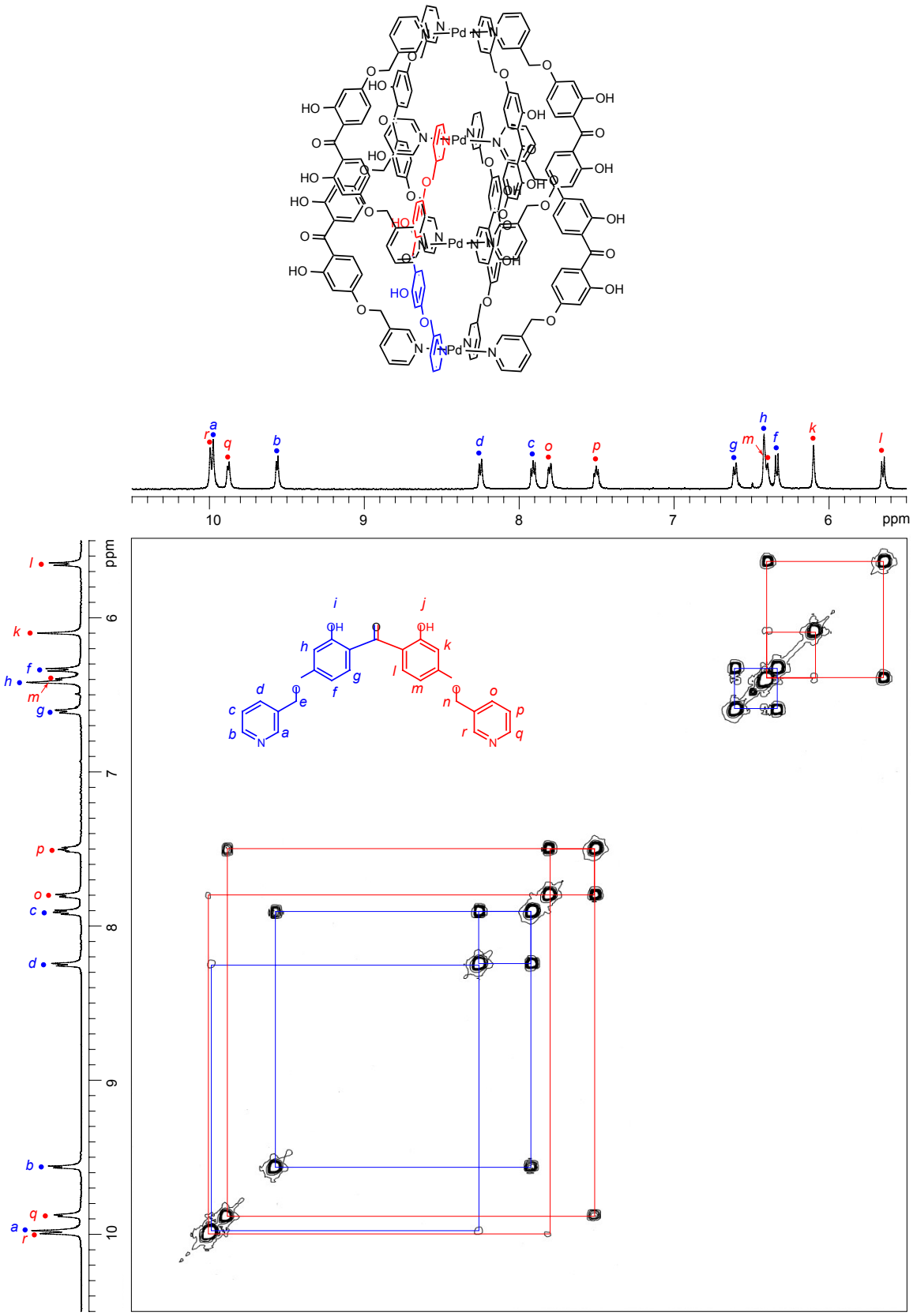

Figure S11. Selected region of ^{1}H-^{1}H COSY spectrum (500 MHz, DMSO-d_6, rt) of **3**.

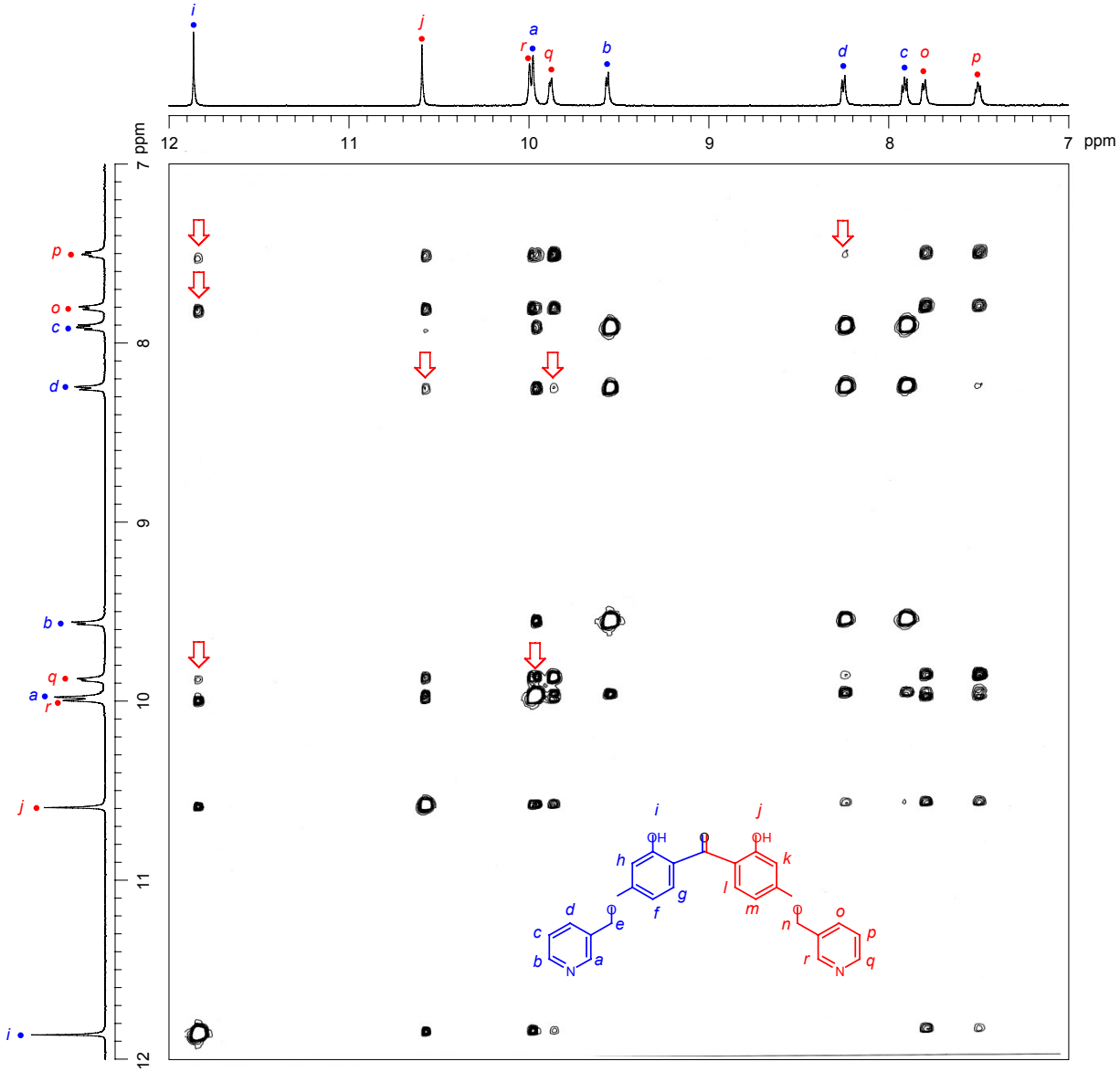

Figure S12. Selected region of NOESY spectrum (500 MHz, DMSO-d_6, rt) of **3**. The red arrows denote NOEs. Mixing time = 0.8 sec.

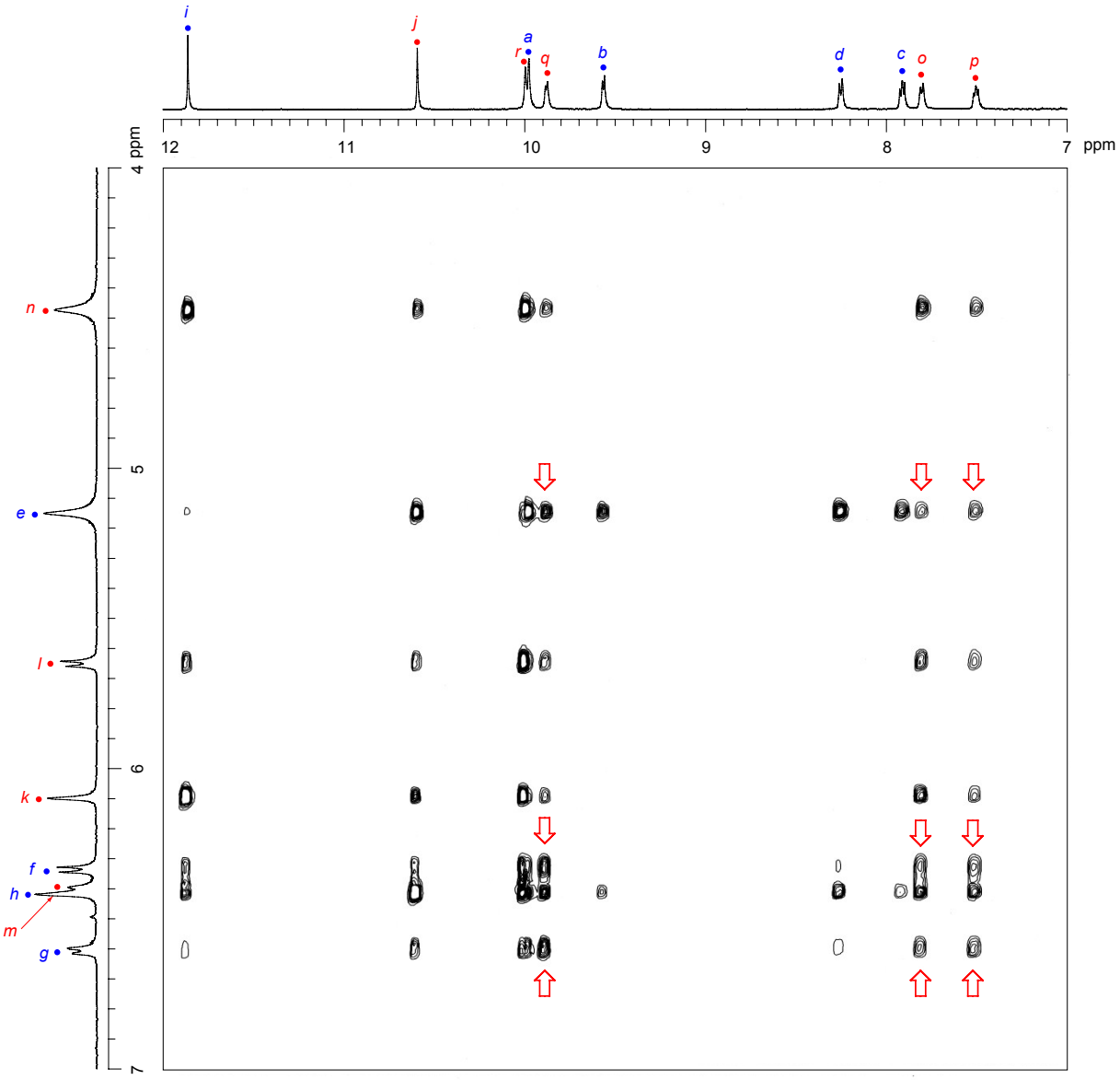

Figure S12. Selected region of NOESY spectrum (500 MHz, DMSO-d_6, rt) of **3** (continued). The red arrows denote NOEs. Mixing time = 0.8 sec.

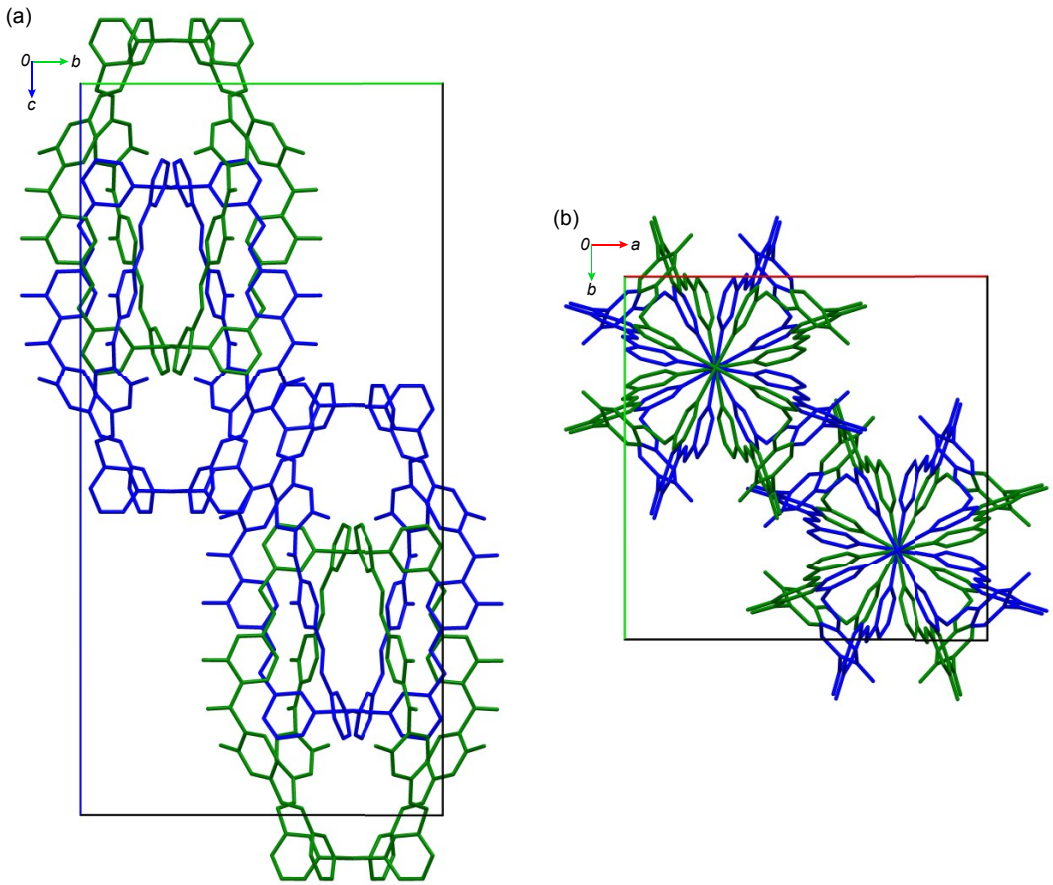

Figure S13. X-ray crystal structure of **3**. The single crystal was crystallized from the DMF solution containing **3** by slow diffusion of 2-propanol vapor into the solution. The one of the two hydroxyl groups on the benzophenone core was disordered over two positions with nearly the same site occupancy factors (0.56 : 0.44).

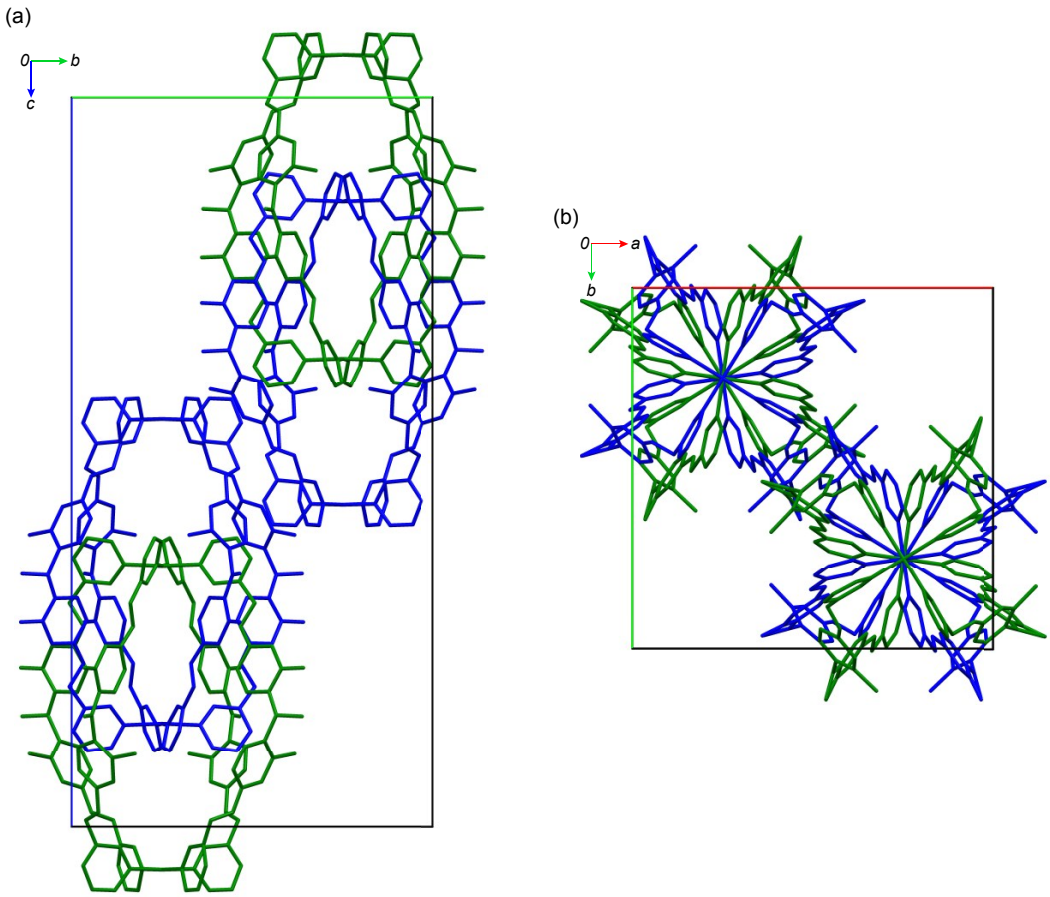

Figure S14. X-ray crystal structure of **3**. The single crystal was crystallized from the DMF solution containing **3** by slow diffusion of 1,4-dioxane vapor into the solution. The benzophenone core was disordered over two positions with nearly the same site occupancy factors (0.52 : 0.48). The atoms of the benzophenone core were refined isotropically.

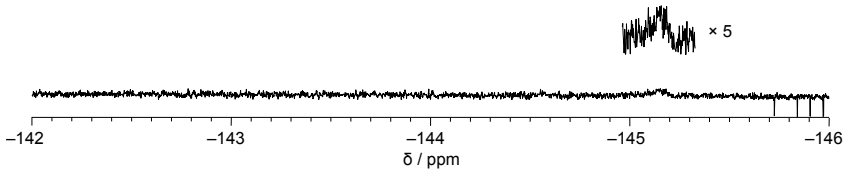

Figure S15. ^{19}F NMR spectrum (470 MHz, DMSO-d_6, rt) of the solution containing monomer **4** and interlocked dimer **3**. The signal at –145.1 ppm may be BF_4^- encapsulated in ***C***.