The hidden features of fullerene rotation in the crystal lattice

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1. Crystal data of the crystal **1**

Table S1. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 1.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	
Formula	$C_{116}H_{55}N_5NiSc_3$	$C_{116}H_{55}N_5NiSc_3$	
Formula weight	1712.24	1712.24	
Color, habit	Black, block	Black, block	
Crystal system	monoclinic	monoclinic	
Space group	$P2_1/c$	$P2_1/c$	
***a*, Å**	17.210(3)	17.210(3)	
***b*, Å**	16.420(3)	16.420(3)	
***c*, Å**	25.760(5)	25.760(5)	
***α*, deg**	90	90	
***β*, deg**	106.31(3)	106.31(3)	
***γ*, deg**	90	90	
Volume, Å^3	6987(3)	6987(3)	
Z	4	4	
***T*, K**	100	100	
Radiation (λ, Å)	Synchrotron Radiation (0.7999)	Synchrotron Radiation (0.7999)	
Unique data (R_{int})	21856 (0.0497)	21856 (0.0497)	
Parameters	1544	2176	
Restraints	438	3591	
Observed data ($I > 2\sigma(I)$)	17902	17902	
R_1[a] (observed data)	0.0805 [c]	0.0670 [c]	0.0667[d]
wR_2[b] (all data)	0.2380 [c]	0.2010 [c]	0.2005[d]
Solvent model	C_7H_8/0.5(C_6H_6)[c]	C_7H_8/ 0.5(C_6H_6)[c]	0.898(C_7H_8)/ 0.479(C_6H_6)[d]
CCDC NO.	2035908	2362043	

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w\left(F_o^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_o^2\right)^2\right]}}$.

[c]Refined with solvent occupancies fixed to 1:0.5. [d]Refined with free solvent occupancies.

2. Crystal data of the crystal **2**

Table S2. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 2.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**		**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	
Formula	$C_{116}H_{55}N_5NiSc_3$		$C_{116}H_{55}N_5NiSc_3$	
Formula weight	1712.24		1712.24	
Color, habit	Black, block		Black, block	
Crystal system	monoclinic		monoclinic	
Space group	$P2_1/c$		$P2_1/c$	
***a*, Å**	17.200(3)		17.260(3)	
***b*, Å**	16.420(3)		16.460(3)	
***c*, Å**	25.750(5)		25.790(5)	
***α*, deg**	90		90	
***β*, deg**	106.34(3)		106.30(3)	
***γ*, deg**	90		90	
Volume, Å^3	6979(3)		7032(3)	
Z	4		4	
***T*, K**	50		80	
Radiation (λ, Å)	Synchrotron Radiation (0.895)		Synchrotron Radiation (0.895)	
Unique data (R_{int})	12045 (0.0934)		9665 (0.1243)	
Parameters	2177		2177	
Restraints	3545		3537	
Observed data ($I > 2\sigma(I)$)	10866		9139	
R_1[a] (observed data)	0.0822 [c]	0.0818[d]	0.0858 [c]	0.0856 [d]
wR_2[b] (all data)	0.2370 [c]	0.2369[d]	0.2419 [c]	0.2425 [d]
Solvent model	C_7H_8/0.5(C_6H_6)[c]	0.915(C_7H_8)/ 0.47(C_6H_6)[d]	C_7H_8/0.5(C_6H_6) [c]	0.94(C_7H_8)/ 0.47(C_6H_6)[d]
CCDC NO.	2362044		2362045	

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w(F_o^2-F_c^2)^2\right]}{\sum\left[w(F_o^2)^2\right]}}$.

[c]Refined with solvent occupancies fixed to 1:0.5. [d]Refined with free solvent occupancies.

3. Crystal data of the crystal **3**

Table S3. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 3.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**		**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	
Formula	$C_{116}H_{55}N_5NiSc_3$		$C_{116}H_{55}N_5NiSc_3$	
Formula weight	1712.24		1712.24	
Color, habit	Black, block		Black, block	
Crystal system	monoclinic		monoclinic	
Space group	$P2_1/c$		$P2_1/c$	
***a*, Å**	17.220(3)		17.240(3)	
***b*, Å**	16.430(3)		16.440(3)	
***c*, Å**	25.760(5)		25.760(5)	
***α*, deg**	90		90	
***β*, deg**	106.30(3)		106.27(3)	
***γ*, deg**	90		90	
Volume, Å^3	6995(3)		7009(3)	
Z	4		4	
***T*, K**	100		110	
Radiation (λ, Å)	Synchrotron Radiation (0.82656)		Synchrotron Radiation (0.82656)	
Unique data (R_{int})	17803 (0.0223)		17823 (0.0281)	
Parameters	2176		2176	
Restraints	3486		3454	
Observed data ($I > 2\sigma(I)$)	16969		16858	
R_1[a] (observed data)	0.0628[c]	0.0624[d]	0.0665[c]	0.0661[d]
wR_2[b] (all data)	0.1813[c]	0.1802[d]	0.1928[c]	0.1921[d]
Solvent model	C_7H_8/0.5(C_6H_6)[c]	0.93(C_7H_8)/ 0.482(C_6H_6)[d]	C_7H_8/0.5(C_6H_6)[c]	0.93(C_7H_8)/ 0.476(C_6H_6)[d]
CCDC NO.	2362046		2362047	

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w\left(F_o^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_o^2\right)^2\right]}}$.

[c]Refined with solvent occupancies fixed to 1:0.5. [d]Refined with free solvent occupancies.

Table S3. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 3_continued.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**		**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	
Formula	$C_{116}H_{55}N_5NiSc_3$		$C_{116}H_{55}N_5NiSc_3$	
Formula weight	1712.24		1712.24	
Color, habit	Black, block		Black, block	
Crystal system	monoclinic		monoclinic	
Space group	$P2_1/c$		$P2_1/c$	
***a*, Å**	17.270(3)		17.300(4)	
***b*, Å**	16.440(3)		16.440(3)	
***c*, Å**	25.740(5)		25.710(5)	
***α*, deg**	90		90	
***β*, deg**	106.22(3)		106.17(3)	
***γ*, deg**	90		90	
Volume, Å^3	7017(3)		7023(3)	
Z	4		4	
***T*, K**	120		130	
Radiation (λ, Å)	Synchrotron Radiation (0.82656)		Synchrotron Radiation (0.82656)	
Unique data (R_{int})	17812 (0.0316)		17809 (0.0358)	
Parameters	2176		2176	
Restraints	3448		3459	
Observed data ($I > 2\sigma(I)$)	16577		16140	
R_1[a] (observed data)	0.0737[c]	0.0733[d]	0.0831[c]	0.0829[d]
wR_2[b] (all data)	0.2178[c]	0.2162[d]	0.2561[c]	0.2557[d]
Solvent model	C_7H_8/0.5(C_6H_6)[c]	0.934(C_7H_8)/ 0.482(C_6H_6)[d]	C_7H_8/0.5(C_6H_6)[c]	0.946(C_7H_8)/ 0.472(C_6H_6)[d]
CCDC NO.	2362048		2362049	

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w\left(F_o^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_o^2\right)^2\right]}}$.

[c]Refined with solvent occupancies fixed to 1:0.5. [d]Refined with free solvent occupancies.

Table S3. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 3_continued.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**		**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	
Formula	$C_{116}H_{55}N_5NiSc_3$		$C_{116}H_{55}N_5NiSc_3$	
Formula weight	1712.24		1712.24	
Color, habit	Black, block		Black, block	
Crystal system	monoclinic		monoclinic	
Space group	$P2_1/c$		$P2_1/c$	
***a*, Å**	17.330(4)		17.340(4)	
***b*, Å**	16.450(3)		16.460(3)	
***c*, Å**	25.680(5)		25.660(5)	
***α*, deg**	90		90	
***β*, deg**	106.10(3)		106.06(3)	
***γ*, deg**	90		90	
Volume, Å^3	7034(3)		7038(3)	
Z	4		4	
***T*, K**	140		150	
Radiation (λ, Å)	Synchrotron Radiation (0.82656)		Synchrotron Radiation (0.82656)	
Unique data (R_{int})	17870 (0.0567)		17870 (0.0389)	
Parameters	2176		2175	
Restraints	3462		3702	
Observed data ($I > 2\sigma(I)$)	15275		14044	
R_1[a] (observed data)	0.0939[c]	0.0936[d]	0.1002[c]	0.1001[d]
wR_2[b] (all data)	0.2929[c]	0.2930[d]	0.3406[c]	0.3410[d]
Solvent model	C_7H_8/0.5(C_6H_6)[c]	0.972(C_7H_8)/ 0.476(C_6H_6)[d]	C_7H_8/0.5(C_6H_6)[c]	0.947(C_7H_8)/ 0.5(C_6H_6)[d]
CCDC NO.	2362050		2362051	

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w\left(F_o^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_o^2\right)^2\right]}}$.

[c]Refined with solvent occupancies fixed to 1:0.5. [d]Refined with free solvent occupancies.

Table S3. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 3_continued.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**		**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**
Formula	$C_{116}H_{55}N_5NiSc_3$		$C_{116}H_{55}N_5NiSc_3$
Formula weight	1712.24		1712.24
Color, habit	Black, block		Black, block
Crystal system	monoclinic		monoclinic
Space group	$P2_1/c$		$C2/m$
***a*, Å**	17.350(4)		25.680(5)
***b*, Å**	16.480(3)		16.500(3)
***c*, Å**	25.660(5)		17.320(4)
***α*, deg**	90		90
***β*, deg**	106.04(3)		106.04(3)
***γ*, deg**	90		90
Volume, Å^3	7051(3)		7053(3)
Z	4		4
***T*, K**	160		170
Radiation (λ, Å)	Synchrotron Radiation (0.82656)		Synchrotron Radiation (0.82656)
Unique data (R_{int})	17763 (0.0286)		9084 (0.0204)
Parameters	2176		899
Restraints	3702		1314
Observed data ($I > 2\sigma(I)$)	12971		7345
R_1[a] (observed data)	0.1101[c]	0.1100[d]	0.1101[c]
wR_2[b] (all data)	0.3955[c]	0.3955[d]	0.3725[c]
Solvent model	C_7H_8/0.5(C_6H_6)[c]	0.959(C_7H_8)/ 0.498(C_6H_6)[d]	C_7H_8/0.5(C_6H_6)[c]
CCDC NO.	2362052		2362053

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w\left(F_o^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_o^2\right)^2\right]}}$.

[c]Refined with solvent occupancies fixed to 1:0.5. [d]Refined with free solvent occupancies.

Table S3. Crystal data_$Sc_3N@C_{2v}$(7854)-C_{70}_crystal 3_continued.

Crystal	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**	**$Sc_3N@C_{70}$·NiOEP·0.5(C_6H_6)·C_7H_8**
Formula	$C_{116}H_{55}N_5NiSc_3$	$C_{116}H_{55}N_5NiSc_3$
Formula weight	1712.24	1712.24
Color, habit	Black, block	Black, block
Crystal system	monoclinic	monoclinic
Space group	*C*2/*m*	*C*2/*m*
***a*, Å**	25.680(5)	25.680(5)
***b*, Å**	16.500(3)	16.510(3)
***c*, Å**	17.350(4)	17.370(4)
***α*, deg**	90	90
***β*, deg**	106.03(3)	106.02(3)
***γ*, deg**	90	90
Volume, Å^3	7066(3)	7078(3)
Z	4	4
***T*, K**	180	190
Radiation (λ, Å)	Synchrotron Radiation (0.82656)	Synchrotron Radiation (0.82656)
Unique data (R_{int})	9170 (0.0198)	9231 (0.0231)
Parameters	899	899
Restraints	1320	1320
Observed data ($I > 2\sigma(I)$)	7506	7793
R_1[a] (observed data)	0.1046	0.1016
wR_2[b] (all data)	0.3555	0.3433
Solvent model	C_7H_8/0.5(C_6H_6)	C_7H_8/0.5(C_6H_6)
CCDC NO.	2362054	2362055

[a]For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum||F_o|-|F_c||}{\sum|F_o|}$. [b]For all data, $wR_2 = \sqrt{\frac{\sum\left[w\left(F_o^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_o^2\right)^2\right]}}$.

4. Crystal site occupancies and temperature relations

Table S4. Site occupancies vs temperature.

Temperature (K)	Site occupancy ratio of fullerene orientations I:II	Site occupancy ratio of NiOEP orientations I:II	Ni-Ni distance (Å) [a]	Crystal label
100	0.7649(17):0.2351(17)	0.8999(9):0.1001(9)	0.6204(6)	**1**
160	0.5:0.5	0.5:0.5 [b]		**1**
220	0.5:0.5	0.5:0.5 [b]		**1**
50	0.793(3):0.207(3)	0.8896(16):0.1104(16)	0.6254(8)	**2**
80	0.744(3):0.256(3)	0.8729(19):0.1271(19)	0.613(2)	**2**
100	0.7885(17):0.2115(17)	0.9266(10):0.0734(10)	0.6107(6)	**3**
110	0.7535(17):0.2465(17)	0.9126(10):0.0874(10)	0.5956(6)	**3**
120	0.7104(18):0.2896(18)	0.8916(11):0.1084(11)	0.5792(7)	**3**
130	0.6604(18):0.3396(18)	0.8514(12):0.1486(12)	0.5529(7)	**3**
140	0.5999(17):0.4001(17)	0.7859(13):0.2141(13)	0.5236(8)	**3**
150	0.5586(14):0.4414(14)	0.7085(14):0.2915(14)	0.489(2)	**3**
160	0.5244(12):0.4756(12)	0.6572(13):0.3428(13)	0.466(2)	**3**
170	0.5:0.5	0.5:0.5 [b]		**3**
180	0.5:0.5	0.5:0.5 [b]		**3**
190	0.5:0.5	0.5:0.5 [b]		**3**

[a]the Ni-Ni distance is distance between two orientations **I** and **II** of NiOEP at low temperatures. [b] the NiOEP shows clear disorder with translational moving character like that observed at low temperatures, the short distance and thermal vibration at high temperature obstacle the stable refinement of NiOEP orientations **I** and **II**, the refinement applied one position (with unit occupancy) with elongated thermal ellipsoids. It is reasonable to assign the value as 0.5:0.5.

5. Sc–N bond length and temperature relations

Table S5. Sc–N bond lengths (Å) vs temperature.

Temperature (K)	Sc–N bonds at main position	Sc–N bonds at minor position	Crystal label
100	2.041(4), 1.978(4), 2.042(3)	2.00(2), 2.00(2), 2.04(2)	**1**
160	2.030(3), 1.996(3), 2.014(3)	2.030(3), 1.996(3), 2.014(3)	**1**
220	2.012(3), 1.978(3), 2.014(3)	2.012(3), 1.978(3), 2.014(3)	**1**
50	2.038(6), 1.975(7), 2.057(7)	2.02(3), 2.00(3), 2.08(3)	**2**
80	2.036(9), 1.983(10), 2.053(10)	2.01(3), 1.96(3), 2.08(3)	**2**
100	2.038(9), 1.989(8), 2.040(7)	2.00(4), 1.96(4), 2.06(4)	**3**
110	2.040(10), 1.990(8), 2.033(8)	1.97(3), 1.95(3), 2.09(3)	**3**
120	2.044(10), 1.990(8), 2.026(8)	1.97(3), 1.94(3), 2.10(3)	**3**
130	2.074(8), 1.970(9), 1.998(7)	1.89(2), 1.99(3), 2.16(3)	**3**
140	2.022(14), 1.954(12), 2.049(13)	2.00(2), 1.96(2), 2.07(2)	**3**
150	1.998(16), 1.941(15), 2.067(15)	2.013(19), 1.96(2), 2.05(2)	**3**
160	1.920(14), 1.98(2), 2.125(15)	2.10(2), 1.95(2), 1.96(2)	**3**
170	2.018(3), 1.989(3), 2.014(3)	2.018(3), 1.989(3), 2.014(3)	**3**
180	2.020(3), 1.989(3), 2.015(3)	2.020(3), 1.989(3), 2.015(3)	**3**
190	2.017(3), 1.986(3), 2.018(3)	2.017(3), 1.986(3), 2.018(3)	**3**

6. Asymmetric unit of the crystal $Sc_3N@C_{70}\cdot NiOEP\cdot 0.5(C_6H_6)\cdot C_7H_8$

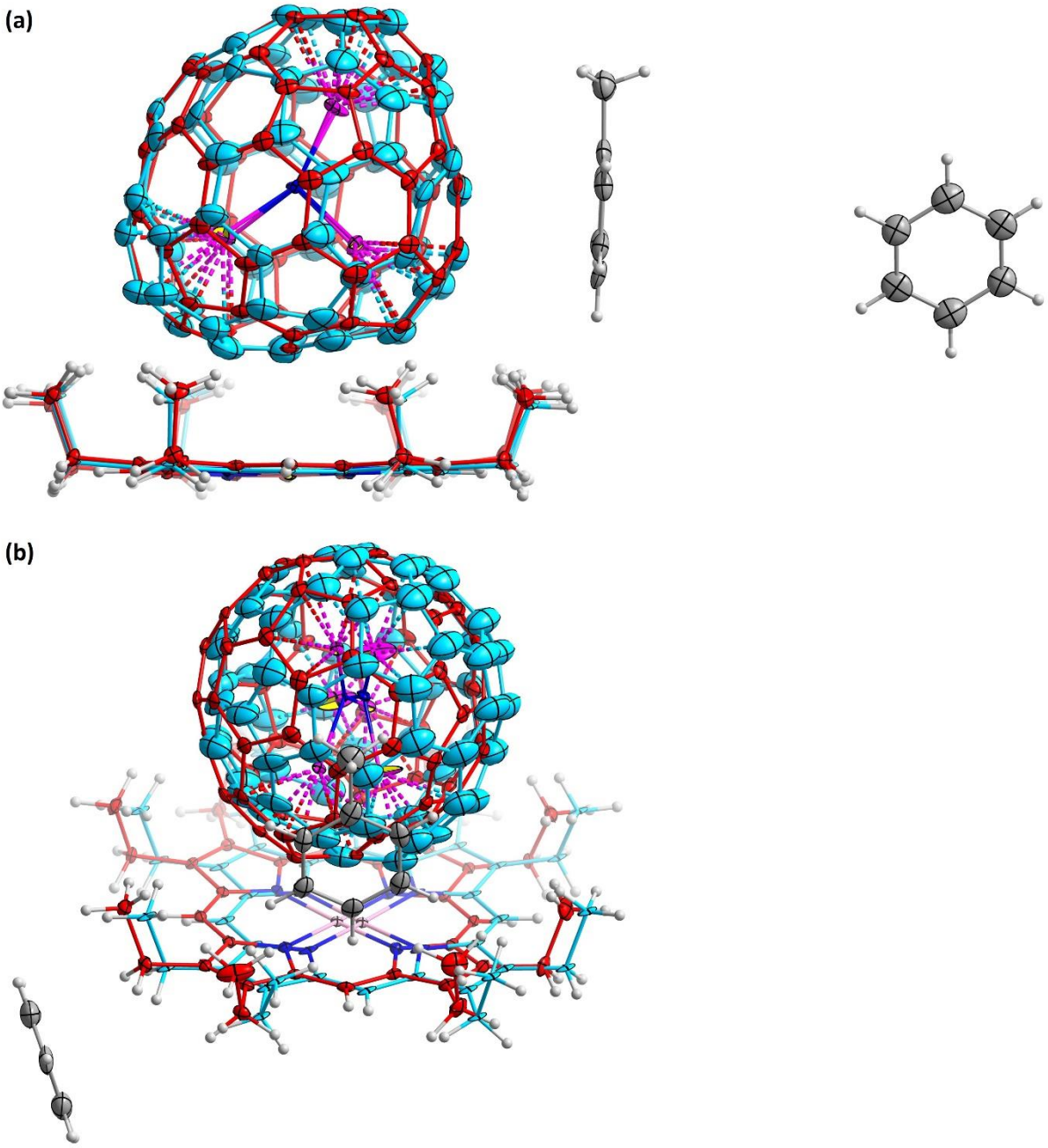

Figure S1. Structures of crystal **2** measured at 50 K. The asymmetric unit was viewed from two perpendicular directions (a, b). The benzene molecule sits on the crystal inversion center; thus, the asymmetric unit contains half benzene. The probability of thermal ellipsoid was set to 30%. Color code: grey for ordered C, red for disordered C with major occupancies, cyan for disordered C with minor occupancies, blue for N, white for H, pink for Sc, and rose for Ni.

7. Cage carbon volume represents site occupancy to show the fullerene rotation driven by temperature

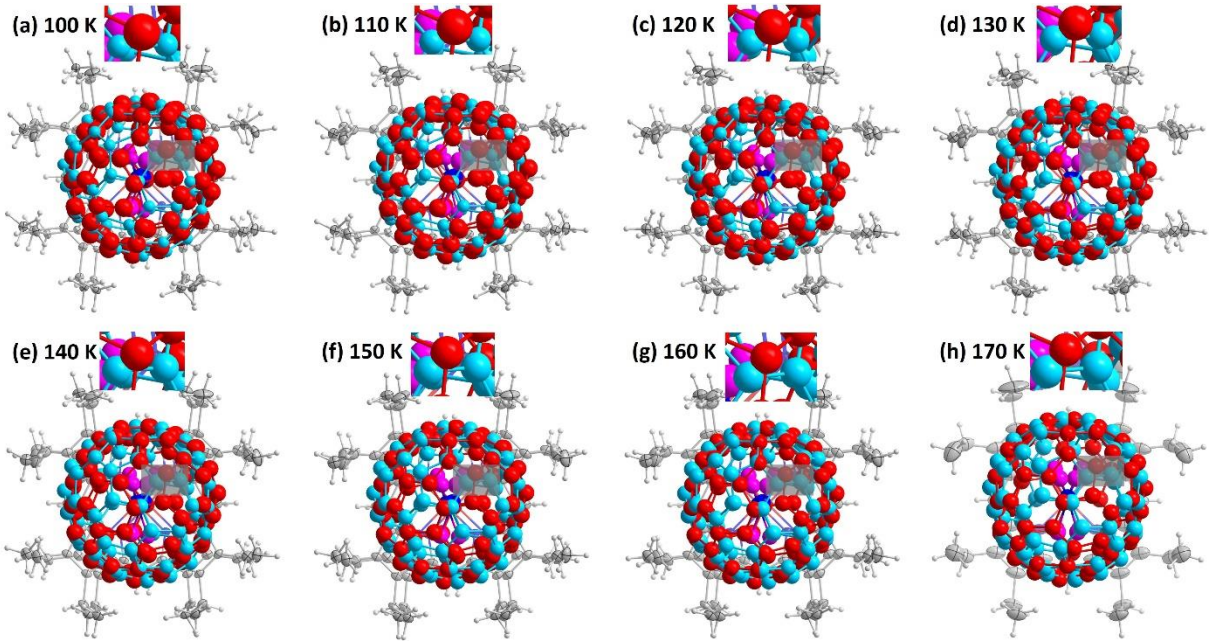

Figure S2. Structures of crystal **3** measured at 100 K (a), 110 K (b), 120 K (c), 130 K (d), 140 K (e), 150 K (f), 160 K (g), and 170 K (h). The solvent molecules were omitted for clarity. The probability of thermal ellipsoid was set to 30%. The two orientations of C_{70} were highlighted with red for **I**, and cyan for **II**, with the volume of the carbon atoms correlated to their site occupancies. The grey masked part was zoomed in to highlight the changes of the site occupancy with temperature. Color code: grey for C in general, blue for N, white for H, pink for Sc, and red for Ni.

8. Site occupancy of NiOEP orientation **I** and the temperature relations

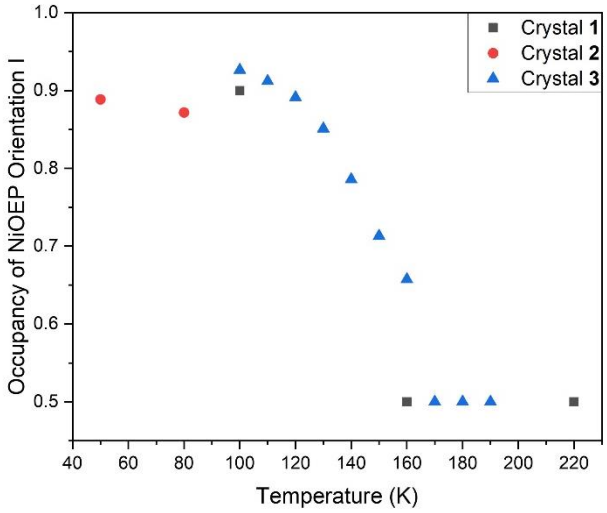

Figure S3. The site occupancy of NiOEP orientation **I** vs measurement temperature relations.

9. The molecules surrounding $Sc_3N@C_{70}$

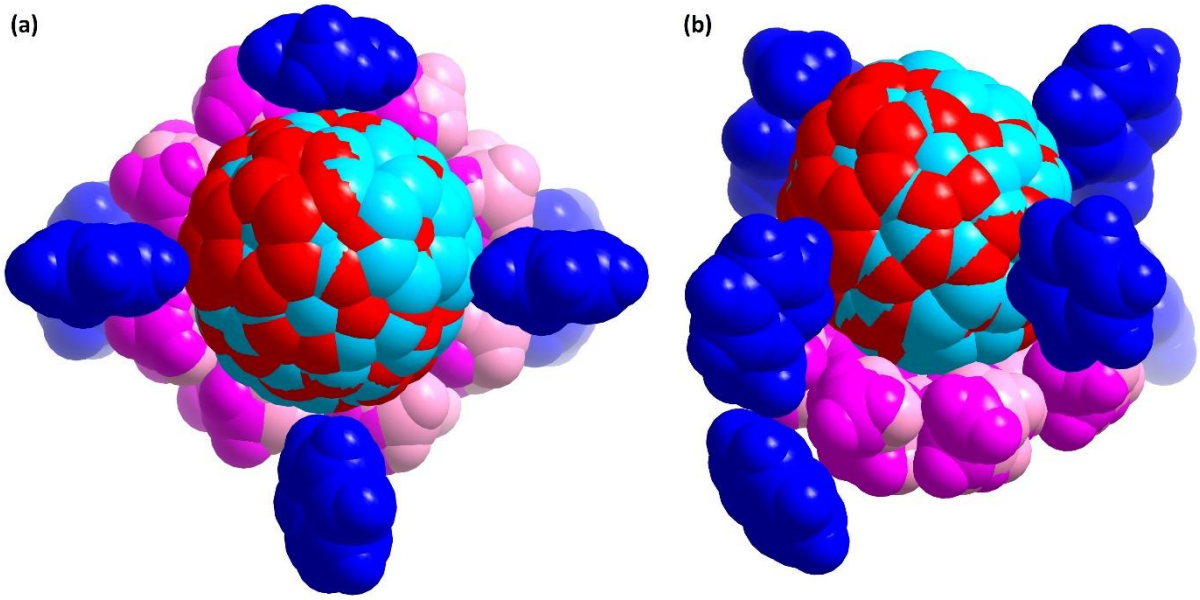

Figure S4. The space-filling structure of crystal **3** at 100 K viewed perpendicular to the NiOEP plane (a) and rotated to a different orientation (b) to show the environment of $Sc_3N@C_{70}$. Color codes: red/cyan for fullerene orientations **I**/**II**, pink/rose for NiOEP orientations **I**/**II**, blue for benzene/toluene molecules interacting with the fullerene cage and NiOEP.

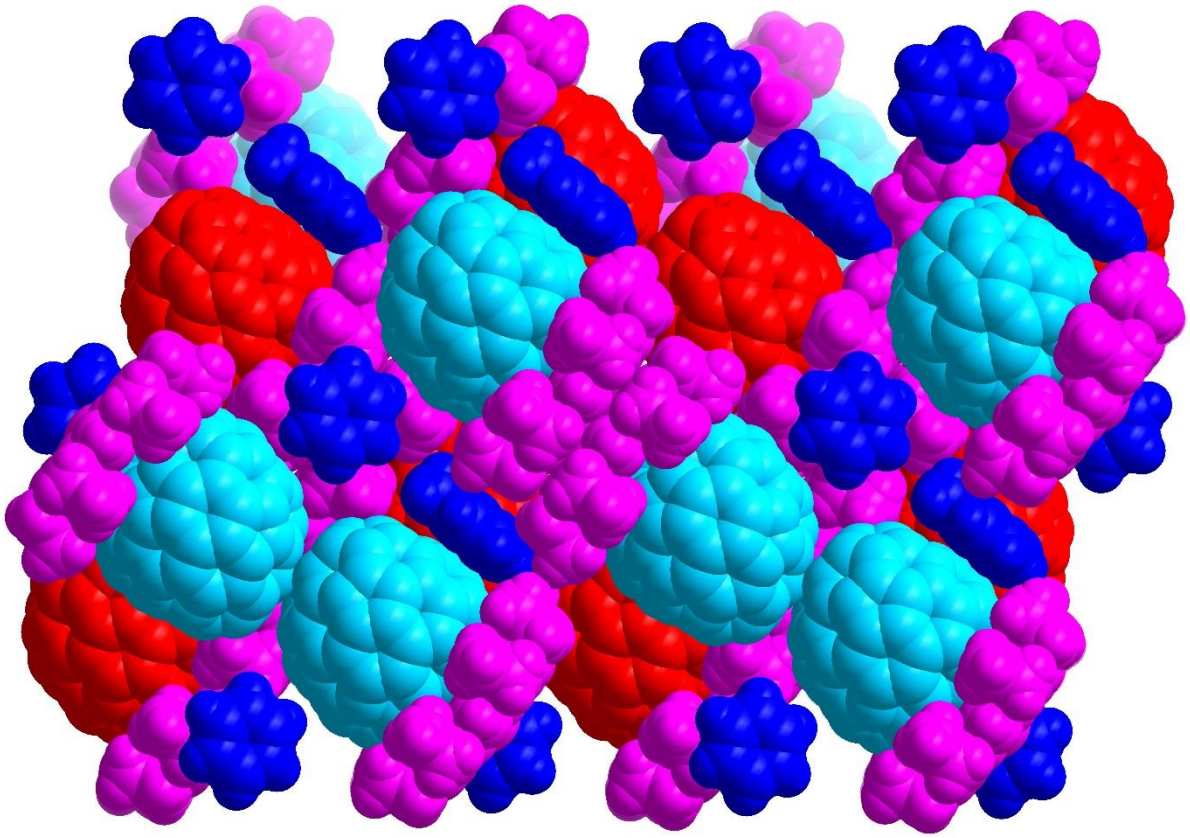

Figure S5. The space-filling structure of crystal **3** at 100 K viewed from the crystal *b* axis to show the environment of $Sc_3N@C_{70}$. Four-unit cells were shown in the figure. Color codes: red/cyan for fullerene orientations **I**/**II**, pink for NiOEP, blue for benzene/toluene molecules.