Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information for

Fullerene rotation dictated by benzene-fullerene interactions

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Contents

1. Crystal data

Table S1. Crystal data_$Dy_2ScN@C_{80}$.

Crystal	**$Dy_2ScN@C_{80}\cdot NiOEP\cdot 2C_6H_6$**	**$Dy_2ScN@C_{80}\cdot NiOEP\cdot 2C_6H_6$**	**$Dy_2ScN@C_{80}\cdot NiOEP\cdot 2C_6H_6$**
Formula	$C_{128}H_{56}Dy_2ScN_5Ni$	C122H50Dy2.07N5Ni	C122H50Dy2.14N5Ni
Formula weight	2092.44	1980.55	1992.94
Colour, habit	Black, block	Black, block	Black, block
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*
***a*, Å**	25.280(5)	25.300(5)	25.350(5)
***b*, Å**	15.030(3)	15.150(3)	15.250(3)
***c*, Å**	39.430(8)	39.590(8)	39.760(8)
***α*, deg**	90	90	90
***β*, deg**	95.26(3)	95.28(3)	95.36(3)
***γ*, deg**	90	90	90
Volume, Å³	14919(5)	15110(5)	15304(5)
Z	8	8	8
***T*, K**	100	180	260
Radiation (λ, Å)	Synchrotron Radiation (0.89429)	Synchrotron Radiation (0.89429)	Synchrotron Radiation (0.89429)
Unique data (R_{int})	15768 (0.0708)	16195 (0.0704)	16487 (0.0993)
Parameters	1296	2002	2032
Restraints	1111	2634	2992
Observed data ($I > 2\sigma(I)$)	13022	13762	13226
R_1[a] (observed data)	0.0453	0.0695	0.1148
wR_2[b] (all data)	0.1229	0.3248	0.4344
CCDC NO.	2330927	2330928	2330929

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

2. Dy_2ScN structure at 100 K

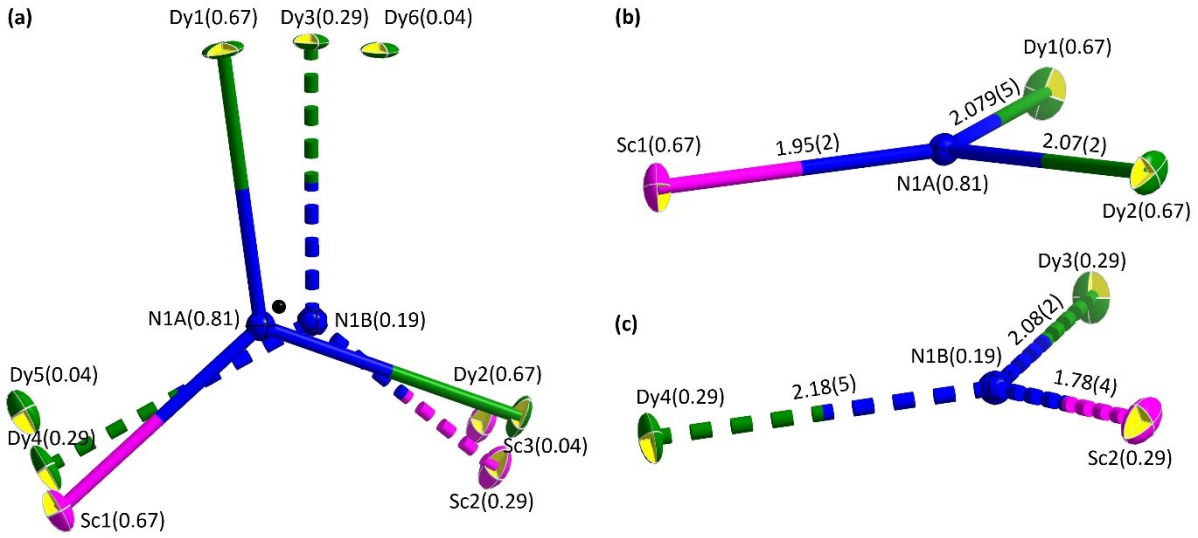

Figure S1. An overview of the Dy_2ScN structure at 100 K is shown with the centroid of C_{80} (black dot in the figure) to mark the displacement of N out of the C_{80} centroid (a). The structure of Dy_2ScN with the major/minor site occupancies is shown in b/c, respectively. The site occupancies with the atom labels and bond lengths (in Å) are shown in the figure. Colour code: blue for N, pink for Sc, and green for Dy. The thermal ellipsoids are set at 30% probability.

3. Relations between two C_{80} orientations at 180 K

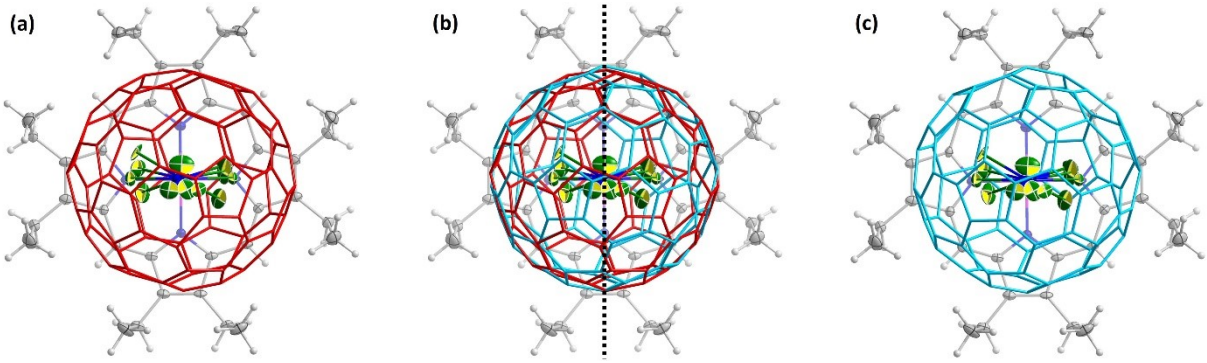

Figure S2. The two orientations (a and c) of C_{80} at 180 K are correlated with a mirror symmetry (perpendicular to the paper and passing through the dotted line in b). Colour code: grey for C, white for H, blue for N, red for Ni, and green for Dy. The thermal ellipsoids are set at 30% probability except for the C_{80}. The C_{80} was highlighted with red/cyan to show the orientations.

4. The environment of $Dy_2ScN@C_{80}$ and $Lu_3N@C_{80}$ in the crystal lattice

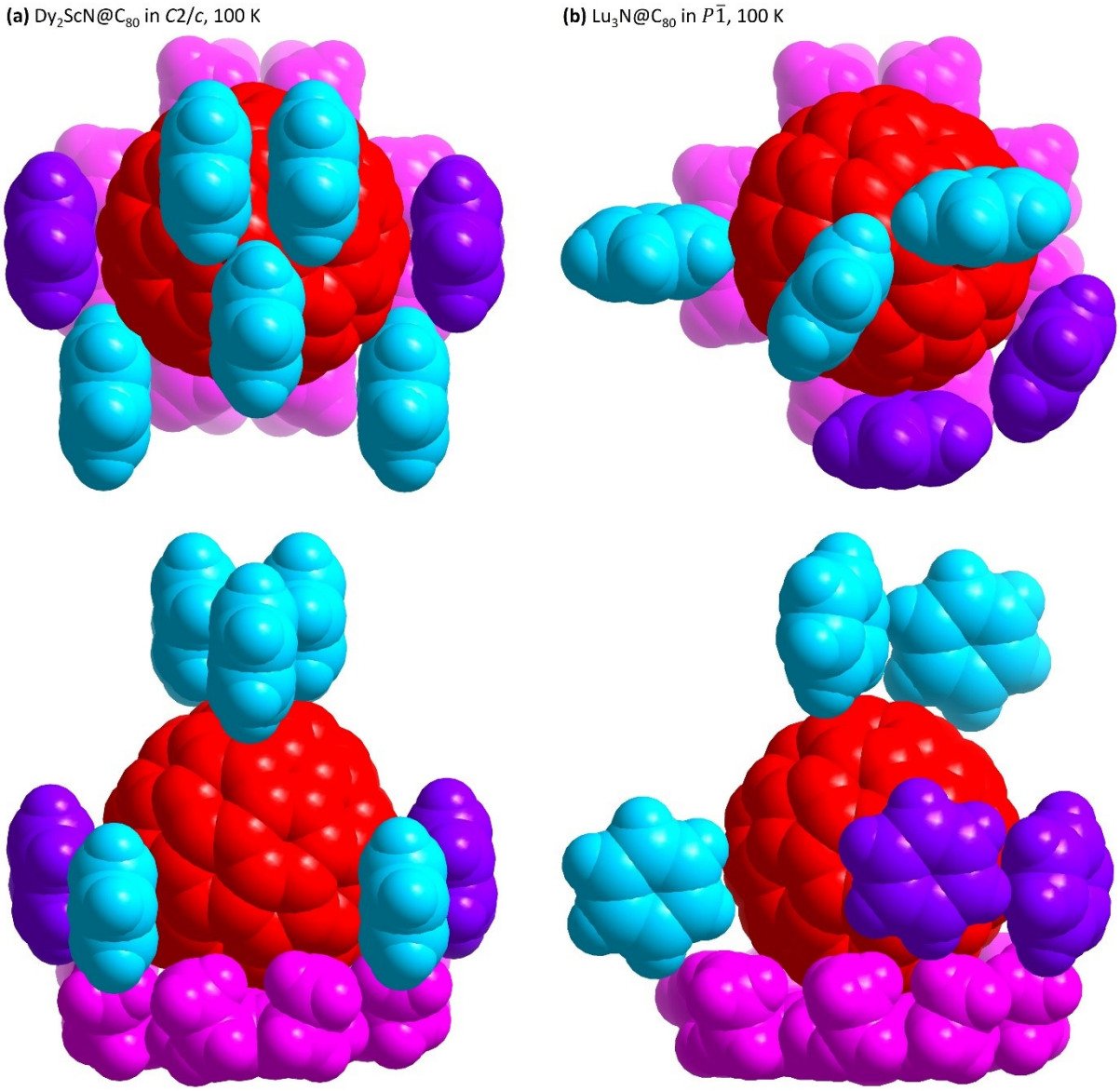

Figure S3. The space-filling structures of $Dy_2ScN@C_{80}\cdot NiOEP\cdot 2C_6H_6$ in *C*2/*c* space group (a) and $Lu_3N@C_{80}\cdot NiOEP\cdot 2C_6H_6$ in $P\bar{1}$ space group (b, data from ref[1]) viewed perpendicular/parallel to the NiOEP plane, upper/lower panels, respectively, observed at 100 K. Colour code: red for fullerene cage, pink for NiOEP, purple for benzene molecules interacting with the fullerene cage through π-π interaction, and cyan for benzene molecules interacting with the fullerene cage through C–H···π interaction.

5. Packing of molecules in the crystal lattice

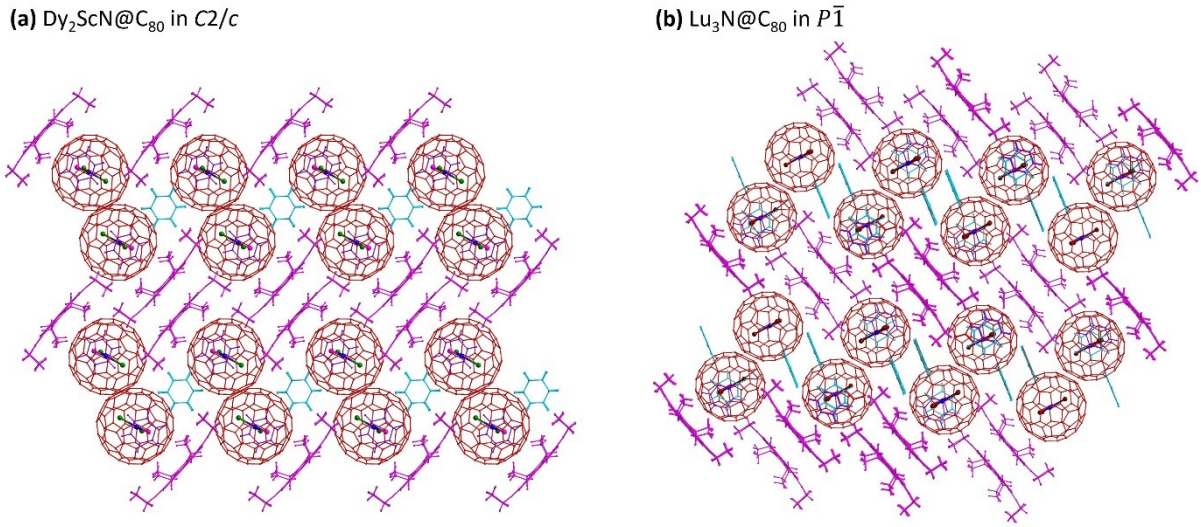

Figure S4. The molecular packings of $Dy_2ScN@C_{80}\cdot NiOEP\cdot 2C_6H_6$ in $C2/c$ space group (a) and $Lu_3N@C_{80}\cdot NiOEP\cdot 2C_6H_6$ in $P\bar{1}$ space group (b; data from ref[1]) were shown for comparison. Colour code: red for the fullerene cage, pink for NiOEP, purple for benzene molecules interacting with the fullerene cage through π-π interaction, and cyan for benzene molecules interacting with the fullerene cage through C–H···π interaction.

6. Thermal ellipsoids of the nitrogen atom at variable temperatures

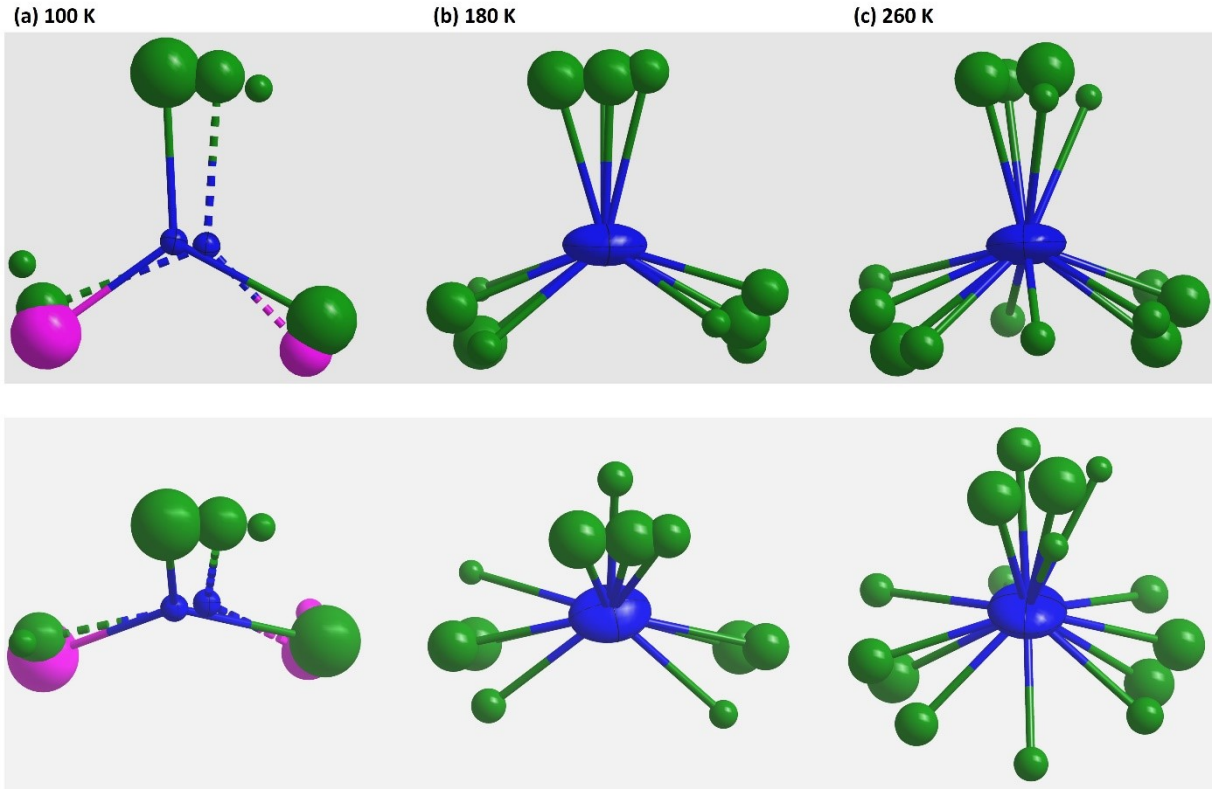

Figure S5. The Dy_2ScN structures of $Dy_2ScN@C_{80}\cdot NiOEP\cdot 2C_6H_6$ observed at variable temperatures of (a) 100, (b) 180 and (c) 260 K. The structures were viewed from two directions (upper/lower panels) to show the thermal ellipsoids' shape clearly. The structures were shown with a metal volume equal to the site occupancy while the thermal ellipsoids of N are set at 70% probability. Colour code: blue for N, pink for Sc, and green for Dy.

7. Metal–Nitrogen bond lengths at high temperatures

Table S2. M–N bond lengths of $Dy_2ScN@C_{80}$ at 180 and 260 K.

Metal position (occupancy) at 180 K	M–N bond lengths (Å) at 180 K	Metal position (occupancy) at 260 K	M–N bond lengths (Å) at 260 K
Dy1 (0.10)	2.07(2)	Dy1 (0.21)	1.90(2)
Dy2 (0.23)	1.963(7)	Dy2 (0.16)	1.94(2)
Dy3 (0.18)	1.983(7)	Dy3 (0.23)	1.97(2)
Dy4 (0.15)	2.153(9)	Dy4 (0.03)	1.93(2)
Dy5 (0.27)	1.949(6)	Dy5 (0.25)	1.93(2)
Dy6 (0.04)	1.85(2)	Dy6 (0.08)	1.85(2)
Dy7 (0.34)	2.052(5)	Dy7 (0.27)	2.01(2)
Dy8 (0.03)	1.95(2)	Dy8 (0.06)	1.96(2)
Dy9 (0.07)	1.900(8)	Dy9 (0.13)	1.855(9)
Dy10 (0.27)	1.873(8)	Dy10 (0.09)	1.92(2)
Dy11 (0.08)	2.008(6)	Dy11 (0.14)	1.99(2)
Dy12 (0.30)	2.014(5)	Dy12 (0.32)	2.019(9)
		Dy13 (0.04)	1.97(2)
		Dy14 (0.07)	1.88(1)
		Dy15 (0.07)	1.91(2)

8. Metal positions relative to NiOEP

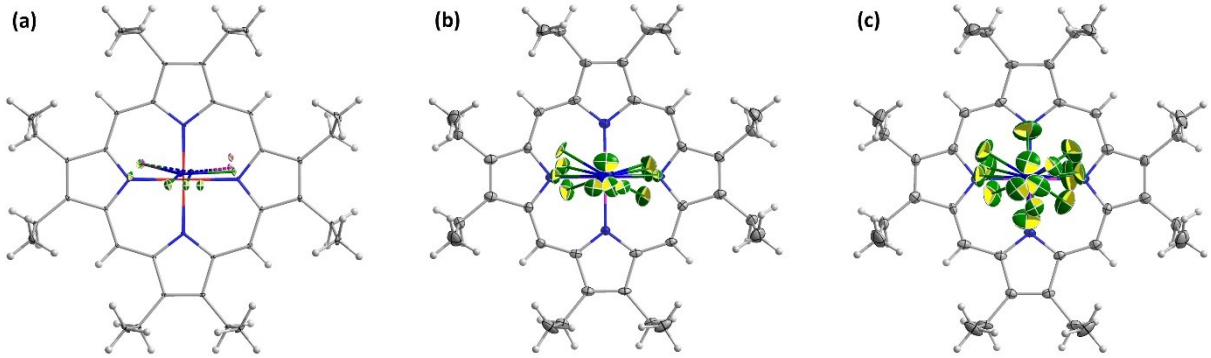

Figure S6. The structures of $Dy_2ScN@C_{80}$·NiOEP·$2C_6H_6$ (a: 100 K, b: 180 K, c: 260 K) are viewed perpendicular to the NiOEP plane. The structures are shown without C_{80} and benzenes for clarity to highlight the metal positions. Colour code: grey for C, white for H, blue for N, red for Ni, pink for Sc, and green for Dy. The thermal ellipsoids are set at 30% probability.

References:

1. F. Liu and L. Spree, Molecular spinning top: visualizing the dynamics of $M_3N@C_{80}$ with variable temperature single crystal X-ray diffraction, *Chem. Commun.*, 2019, **55**, 13000-13003.