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Electronic Supplementary Information

UN@C_2(13)-C_{84}: A Diatomic Cluster with a U≡N Triple Bond inside a C_{84} Fullerene Cage

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High-performance liquid chromatography (HPLC) Separation Process of UN@C_2(13)-C_{84}. As shown in Fig. S1, the first step was performed on a Buckyprep-M column (20 mm × 250 mm, Cosmosil Nacalai Tesque) with toluene as the mobile phase with a flow rate of 10 mL/min. The fraction from 28 to 35 min was re-injected into a Buckyprep column (10 mm × 250 mm, Cosmosil Nacalai Tesque) for the second step separation using toluene as the eluent with a flow rate of 4 mL/min. The fraction containing UN@C_2(13)-C_{84} was collected. The third step of separation was conducted on a 5PBB column (10 mm × 250 mm, Cosmosil Nacalai Tesque) using toluene as the eluent with a flow rate of 4 mL/min. The fraction containing UN@C_2(13)-C_{84} was collected. The fourth stage was conducted on a Buckyprep-M column (10 mm × 250 mm, Cosmosil Nacalai Tesque) using toluene as the eluent with a flow rate of 4 mL/min. The fraction containing UN@C_2(13)-C_{84} was collected and re-injected into a Buckyprep column with a recycling method (10 mm × 250 mm, Cosmosil Nacalai Tesque) using toluene as the eluent with a flow rate of 4 mL/min in the fifth stage. The purity of the isolated UN@C_2(13)-C_{84} was then reconfirmed by chromatography on a Buckyprep column (10 mm × 250 mm, Cosmosil Nacalai Tesque) with toluene with a flow rate of 4.0 mL/min, along with the MALDI-TOF mass spectrometry under positive-ion mode (Fig. 1).

In total 2.02 g of graphite powder and 1.58 g of U_3O_8 (molar ratio of C:U = 30:1) were packed in each rod. On average ca. 0.1 mg of crude fullerene mixture per rod was obtained and totally 300 carbon rods were vaporized in this work.

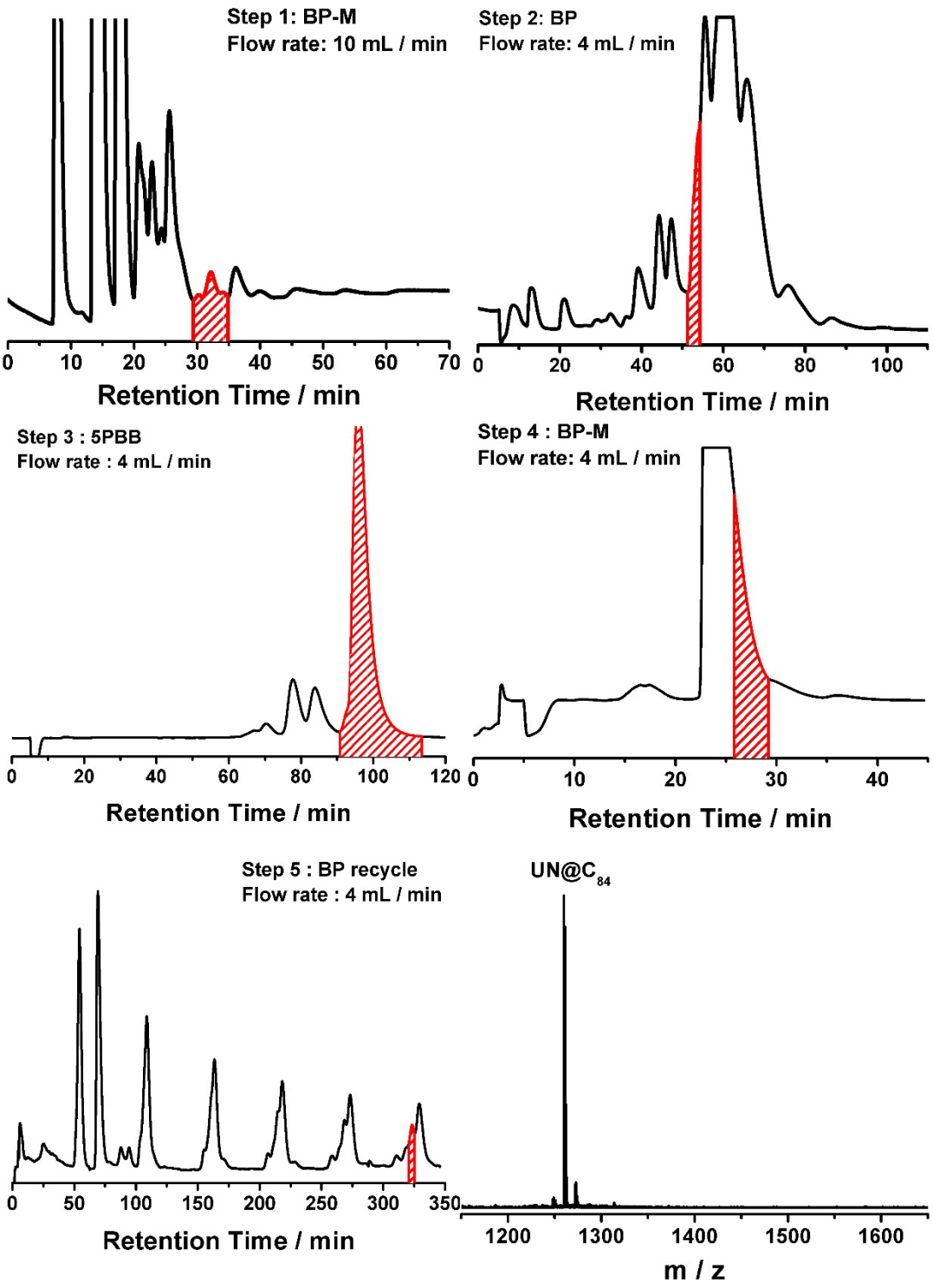

Fig. S1. HPLC separation process of UN@C_2(13)-C_{84} and the corresponding mass spectrum of the purified sample.

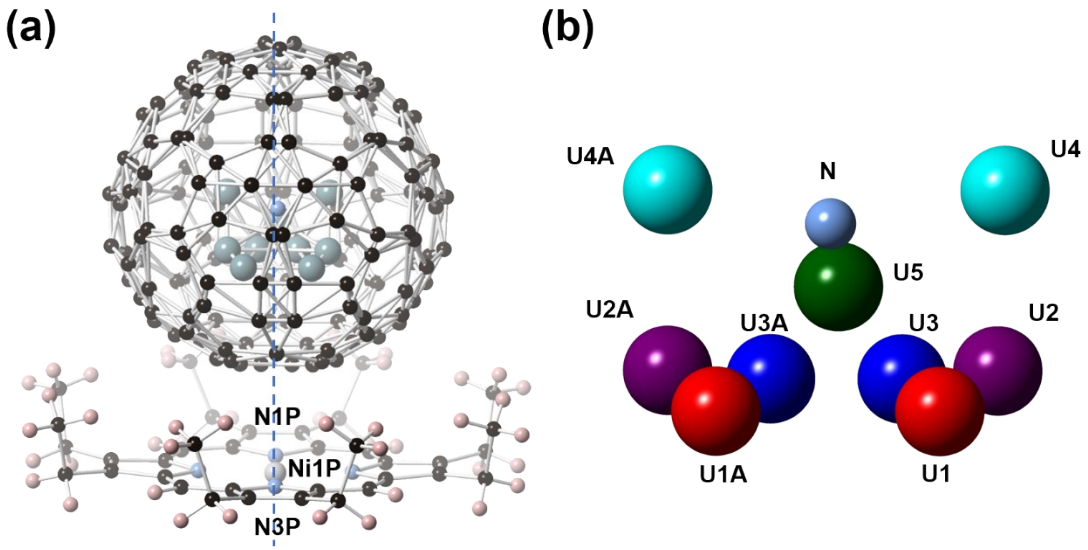

Fig. S2. (a) Ball-and-stick representation of the disordered carbon cage and U sites in UN@C_2(13)-C_{84}. (b) Detailed illustration of all U and N sites. The N atom is fully ordered and precisely positioned on the crystallographic mirror plane. In total, nine disordered sites are identified for the U atom. For one orientation, five disordered U sites (U1, U2, U3, U4, and U5) are shown, with fractional occupancies of 0.205, 0.191, 0.045, 0.042, and 0.035, respectively. Notably, the U5 site lies on the crystallographic mirror plane. For the mirror-generated counterpart orientation, four disordered U sites (U1A, U2A, U3A, and U4A) are presented, each with the same fractional occupancy as their corresponding sites in the primary orientation.

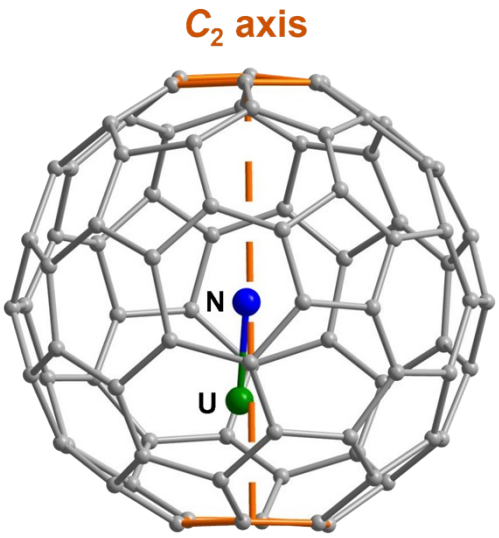

Fig. S3. Density functional theory (DFT)-optimized structure of UN@C_2(13)-C_{84}. The orange dashed lines represent the C_2 axis of the carbon cages.

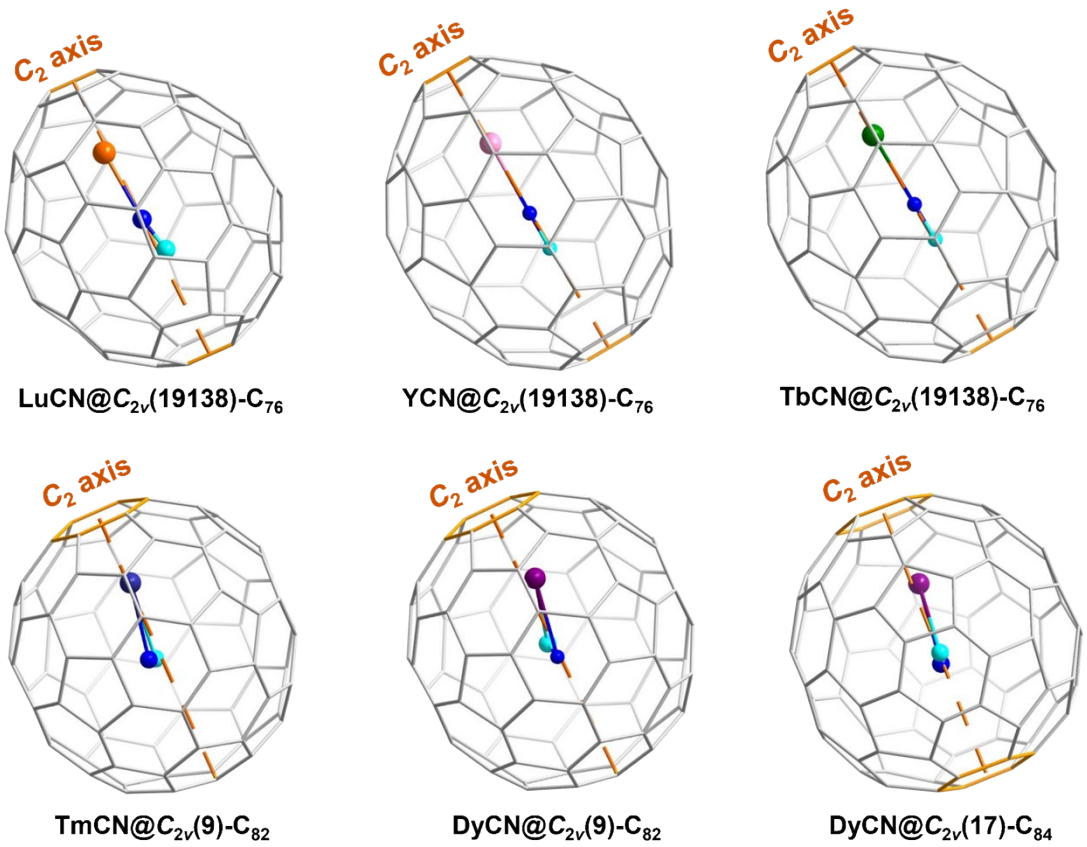

Fig. S4. Positional relationship between the encapsulated metal atom in mononuclear clusterfullerenes and the C_2 axis of C_{2v}-symmetry carbon cages. Examples include LuCN@C_{2v}(19138)-C_{76}, YCN@C_{2v}(19138)-C_{76}, TbCN@C_{2v}(19138)-C_{76}, TmCN@C_{2v}(9)-C_{82}, DyCN@C_{2v}(9)-C_{82}, and DyCN@C_{2v}(17)-C_{84}. The orange dashed lines represent the C_2 axis of the carbon cages.

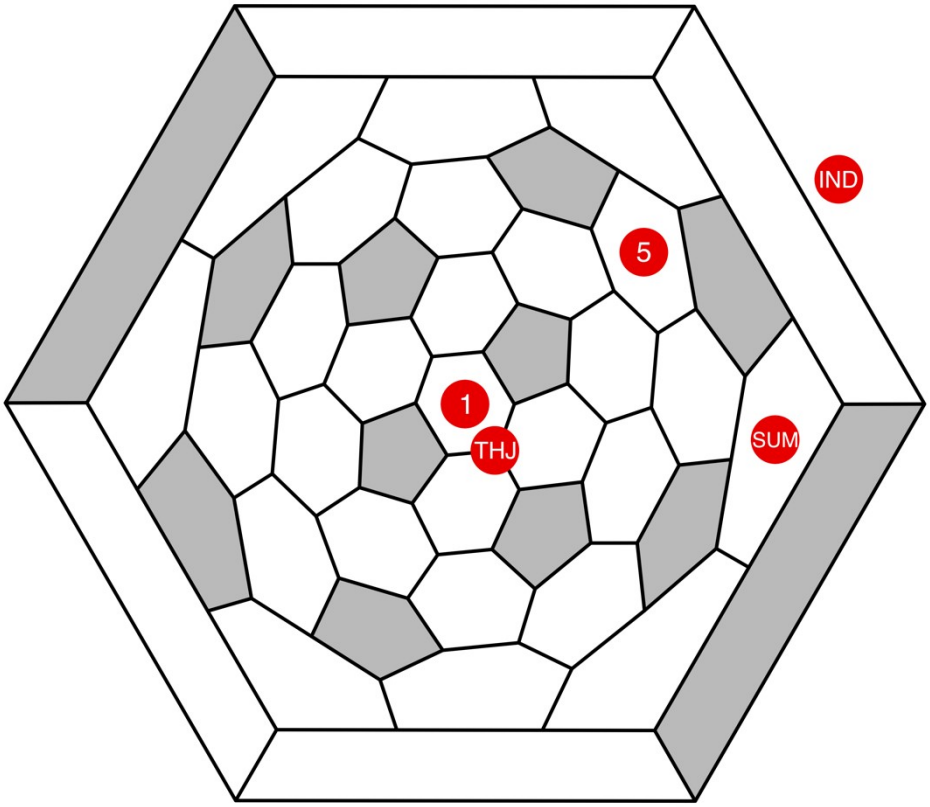

Fig. S5. Schlegel diagram with different computed positions for U in UN@C_2(13)-C_{84}.

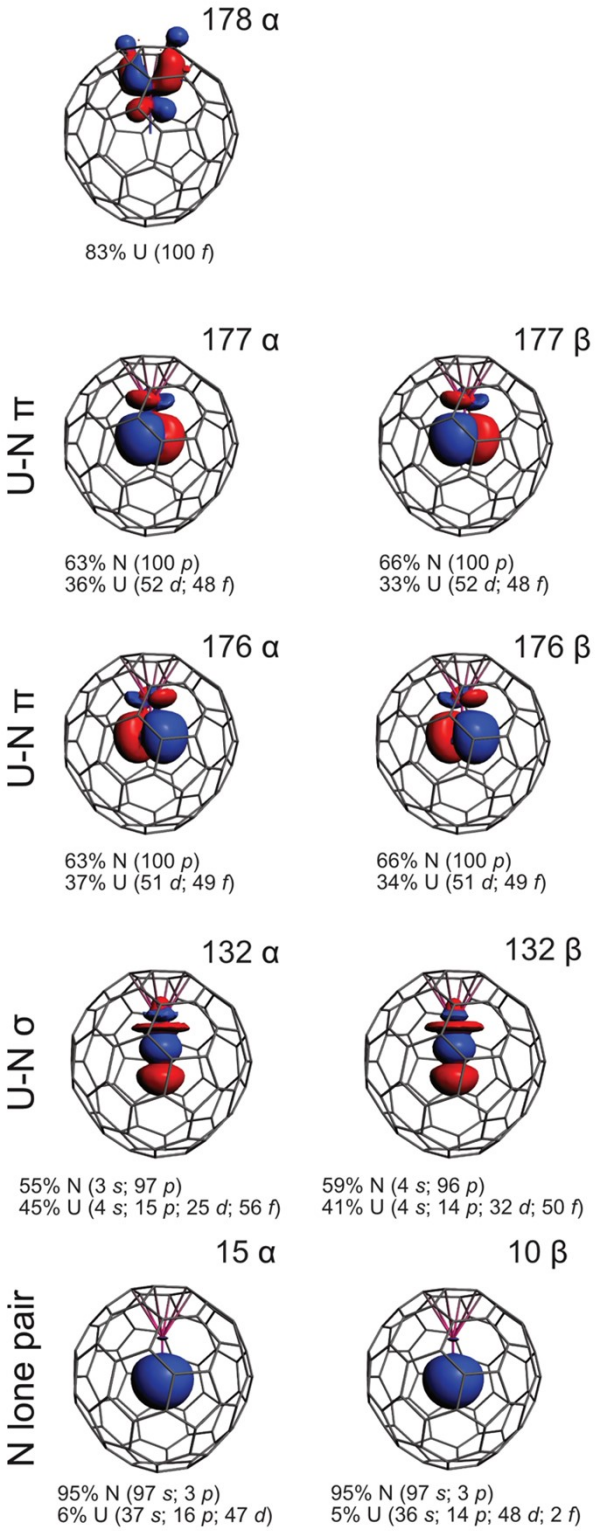

Fig. S6. Pipek-Mezey localized molecular orbitals for UN@C_2(13)-C_{84}. For each molecular orbital, the percentages of U and N contributions are shown. In parenthesis, the percentages of each atomic orbital type. Orbitals participating in the U-N bond are marked as σ and π.

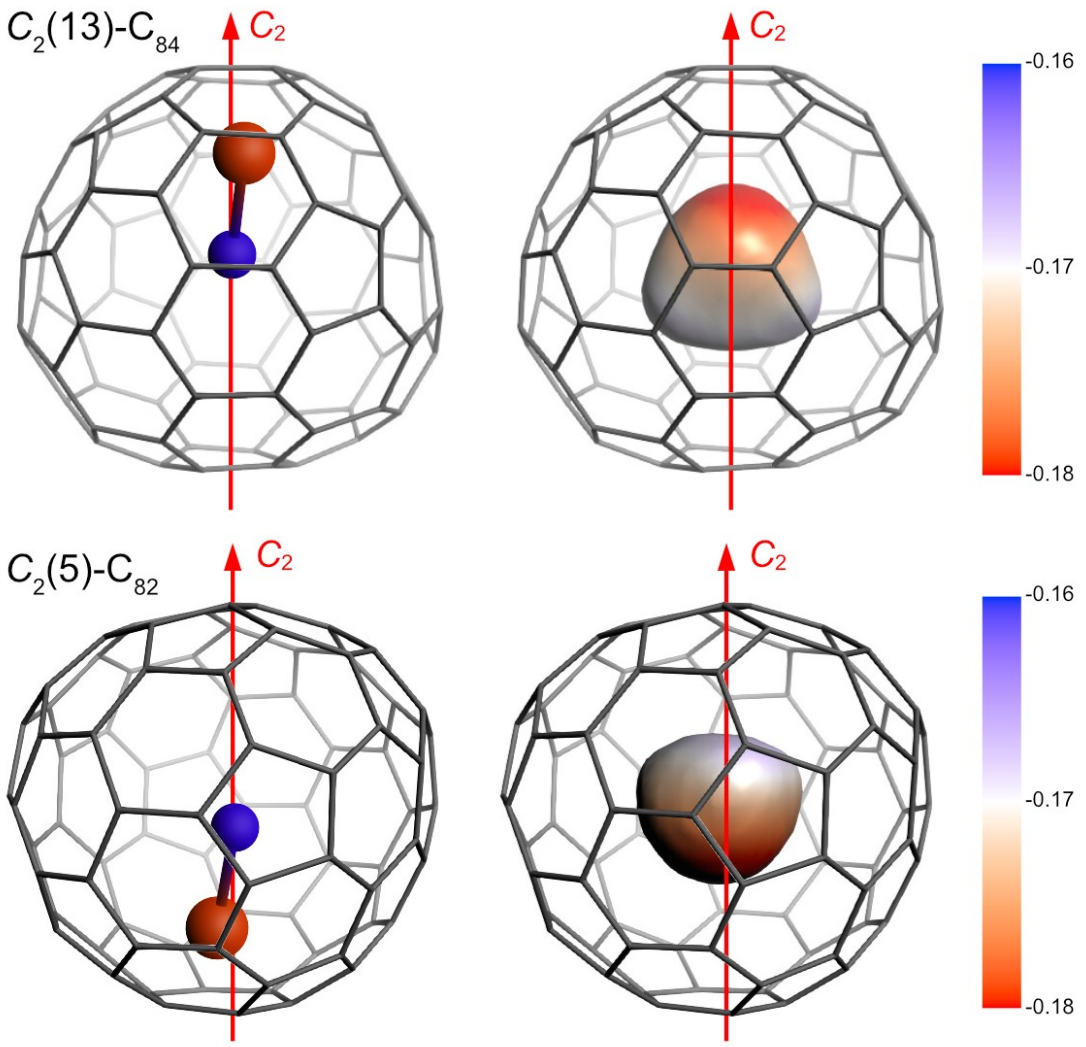

Fig. S7. Representation of the molecular electrostatic potential in the interior of the $C_2(13)$-C_{84}^{2-} and $C_2(5)$-C_{84}^{2-} dianions (in atomic units) together with position of the UN cluster.

Table S1. Closest U-Cage distances (Å) in UN@C_2(13)-C_{84}.

Labeling	U1-C1	U1-C6	U1-C7	U1-C8	U1-C9	U1-C10
Distance	2.746(18)	2.642(15)	2.429(14)	2.411(22)	2.566(17)	2.685(15)

Table S2 Crystallographic information for UN@C_2(13)-C_{84}.

UN@C_2(13)-C_{84}			
Formula weight	1930.45	ρ, g·cm^{-1}	1.679
Crystal system	monoclinic	T, K	120(2)
Space group	$C2/m$ (No.12)	Radiation (λ, Å)	1.34138
Crystal size, mm^3	0.12×0.07×0.05	θ, deg	3.045-55.895
a, Å	25.3984(10)	R_1/wR_2 (all data)	0.1618/0.2422
b, Å	15.1347(6)	R_1/wR_2 ($I>2\sigma(I)$)	0.0993/0.2756
c, Å	19.9768(7)	Unique data	4827
α, deg	90	Observed data	7793
β, deg	96.144(2)	R_{int}	0.0951
γ, deg	90	GOF indicator	1.081
Volume, Å^3	7634.9(5)	Parameters	1033
Z	4	CCDC	2235367

$R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $wR_2=[\sum w(F_o^2-F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

XYZ coordinates of DFT-optimized UN@C_2(13)-C_{84}

U	16.754609	6.759113	5.200768	C	14.252676	7.420494	0.860041
N	17.377020	7.567301	3.759950	C	13.508089	8.157549	1.831312
C	16.525541	7.149585	-0.222459	C	13.795910	9.456099	2.059730
C	19.044283	7.028508	-0.049656	C	13.753898	9.990350	3.346813
C	17.878997	7.724700	-0.337661	C	13.619510	9.139786	4.524652
C	18.123777	8.968764	-0.039724	C	14.339137	9.510584	5.720368
C	15.983850	4.092397	5.589276	C	15.185130	10.685028	5.718382
C	16.030212	3.691330	4.190964	C	16.442299	10.753135	6.379800
C	15.109254	4.109044	3.237570	C	16.775767	9.872301	7.269635
C	14.013756	5.023175	3.599065	C	18.127875	9.428858	7.426547
C	13.940121	5.445430	4.967583	C	19.182438	9.960082	6.548630
C	14.884127	4.974744	5.942827	C	20.280802	9.064114	6.278501
C	15.128674	6.047788	6.856497	C	20.237167	7.688379	6.707529
C	16.353920	6.261186	7.484148	C	20.973970	6.886244	5.690575
C	17.403170	5.357650	7.221965	C	21.483844	7.830643	4.705400
C	17.236392	4.304281	6.222887	C	21.625313	7.420495	3.438180
C	18.533085	4.098451	5.549551	C	21.324782	6.141622	3.021069
C	18.579449	3.782137	4.151240	C	20.932499	6.229402	1.710152
C	17.292339	3.543011	3.579203	C	20.013786	5.403052	1.231468
C	17.124259	3.841162	2.214656	C	19.147446	5.788984	0.266156
C	15.777735	4.169583	1.982266	C	17.071219	9.881380	0.347592
C	15.442871	5.227491	1.010996	C	15.695810	9.422802	0.407179
C	14.280157	6.061407	1.289069	C	14.780247	10.118994	1.338725
C	13.622452	5.981195	2.562248	C	15.280167	11.120904	2.145138
C	13.190717	7.294878	2.915799	C	14.630960	11.042205	3.386537
C	13.266106	7.768591	4.268428	C	15.315722	11.344897	4.528625
C	13.632892	6.781815	5.273465	C	16.645010	11.801962	4.449175
C	14.329284	7.172288	6.425483	C	17.348028	11.373653	5.539620
C	14.686673	8.504133	6.715474	C	18.754317	10.890860	5.499896
C	15.864364	8.731152	7.478190	C	19.457955	10.981667	4.224730
C	16.682440	7.567302	7.853589	C	20.600137	10.123535	3.948643
C	18.094827	8.018313	7.851603	C	20.947007	9.139786	4.973543
C	19.134284	7.135966	7.444424	C	20.726733	9.654362	2.536427
C	18.801412	5.779906	7.186212	C	21.368006	8.310409	2.383487
C	19.485143	5.024688	6.119602	C	20.919378	7.567300	1.312904
C	20.560565	5.545319	5.331066	C	19.987327	7.938098	0.438959
C	20.602465	5.219925	3.950629	C	19.385915	9.068652	0.528340
C	19.618910	4.314875	3.342840	C	19.754147	10.053915	1.567143
C	19.398800	4.473788	1.942542	C	18.742353	11.022529	1.835285
C	18.113915	4.337577	1.467831	C	17.483423	10.963504	1.237427
C	17.924279	5.207816	0.468752	C	16.595661	11.500782	2.099455
C	16.539708	5.726933	0.188693	C	17.282936	11.868554	3.265377
C	15.416678	7.988042	0.168830	C	18.598747	11.493216	3.122368