Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

M@C_2(10612)-C_{72} (M = Ce, Gd): Synthesis and Characterization of Open-Shell Paramagnetic Mono-metallofullerenes

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HPLC separation process of Ce@C_2(10612)-C_{72}

Toluene was employed as the mobile phase for Ce@C_2(10612)-C_{72} purification in a series of HPLC separations. The process commenced with the injection onto a Buckyprep-M column (20 mm × 250 mm), as depicted in Figure S1a. From this run, the eluent collected between 27.5 and 32.7 minutes (indicated in red) was identified to contain Ce@C_2(10612)-C_{72} and was carefully collected for reprocessing. In the next phase, this fraction was introduced into a Buckyprep column (10 mm × 250 mm), where the fraction spanning 49.4 to 54.3 minutes (highlighted in pink) was collected (Figure S1b). The final purification step was carried out using a 5PBB column (10 mm × 250 mm). The fraction eluting from 18.1 to 22.4 minutes (marked in orange) was collected, yielding the pure Ce@C_2(10612)-C_{72}. The purity of the isolated Ce@C_2(10612)-C_{72} is confirmed by the mass spectrum shown in Figure S1d.

HPLC separation process of Gd@C_2(10612)-C_{72}

An analogous purification strategy was applied for Gd@C_2(10612)-C_{72}. Initially, a Buckyprep-M column (20 mm × 250 mm) was used with toluene as the mobile phase, and the fraction between 21 and 22.5 minutes (displayed in blue) containing Gd@C_2(10612)-C_{72} was collected (Figure S2a). This fraction was then injected into a 5PYE column (10 mm × 250 mm) for further refinement, where the fraction eluting from 37.1 to 50 minutes (marked in purple) was collected (Figure S2b). In the final purification step, the sample was subjected to separation on a 5PBB column (10 mm × 250 mm), and the fraction collected between 25.5 and 31.4 minutes (highlighted in cyan) represented the pure Gd@C_2(10612)-C_{72}. The mass spectrum in Figure S2d confirms the high purity of Gd@C_2(10612)-C_{72}.

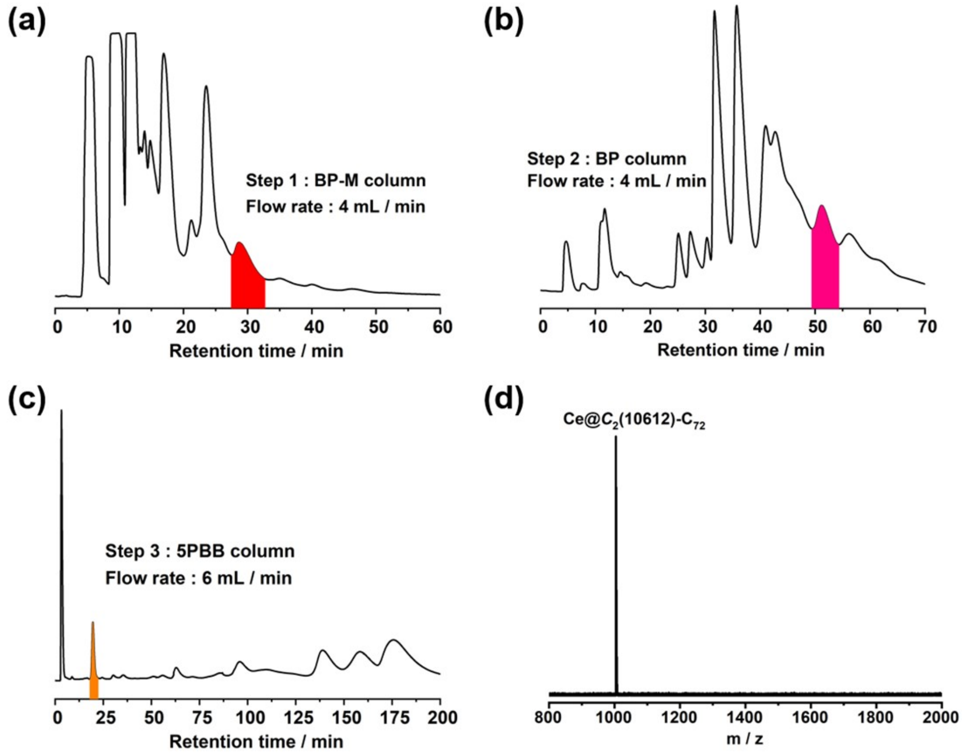

Figure S1. (a-c) HPLC profiles showing the isolation procedures of Ce@C_2(10612)-C_{72}. (d) The MALDI-TOF mass spectrum of the purified Ce@C_2(10612)-C_{72}.

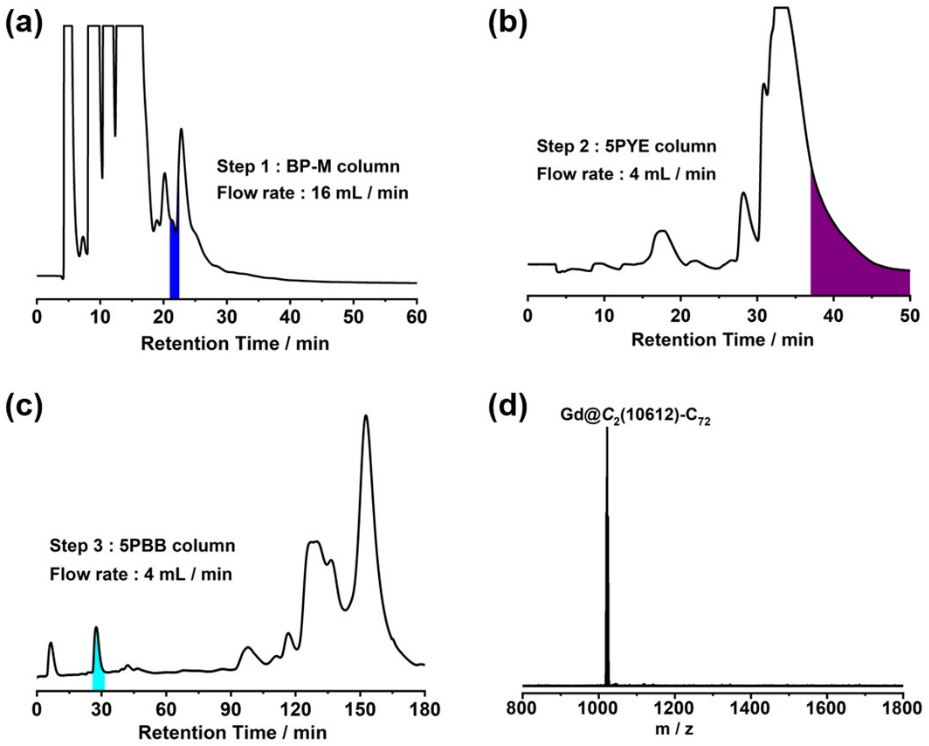

Figure S2. (a-d) HPLC profiles showing the isolation procedures of Gd@C_2(10612)-C_{72}. (e) The MALDI-TOF mass spectrum of the purified Gd@C_2(10612)-C_{72}.

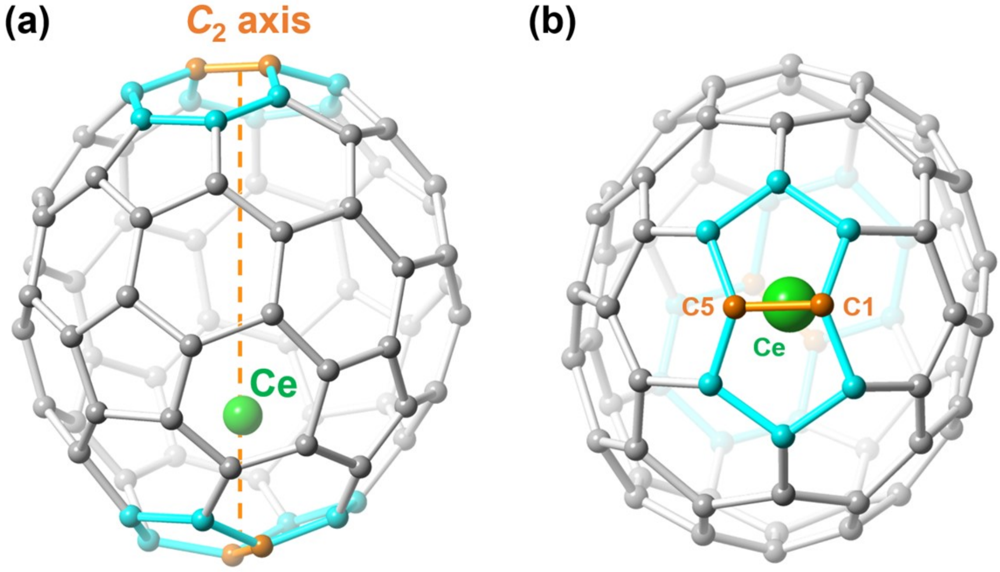

Figure S3. The ball and stick model of Ce@C_2(10612)-C_{72} with (a) front side view and (b) front view. The C_2 axis is highlighted in orange, and the pentalene motif and as-indacene fragment of the opposite end are highlighted in cyan.

Table S1. Crystallographic information of Ce@C_2(10612)-C_{72}

	Ce@C_2(10612)-C_{72} Ni^{II}(OEP)
Empirical formula	$C_{150}H_{94}CeN_8Ni_2$
Formula weight	2265.87
Radiation	Mo Kα (λ = 0.71073 Å)
Crystal system	monoclinic
Space group	$C2/c$
a, Å	20.3263(8)
b, Å	20.7023(10)
c, Å	23.2603(10)
α, deg	90
β, deg	92.4240(10)
γ, deg	90
Volume, Å^3	9779.2(7)
Crystal size, mm^3	0.08×0.06×0.05
Z	4
T, K	100(2)
F(000)	4656
ρ, g·cm^{-3}	1.539
2θ, deg	3.506-50.704
R_1(all data)	0.1317
wR_2(all data)	0.2583
$R_1(I \geq 2.0\sigma(I))$	0.0861
$wR_2(I \geq 2.0\sigma(I))$	0.2138
parameters	1439
Goodness-of-fit indicator	1.011
R_{int}	0.0984
CCDC	2441979

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