Dimerization of Radical-Anions: Nitride Clusterfullerenes vs Empty Fullerenes

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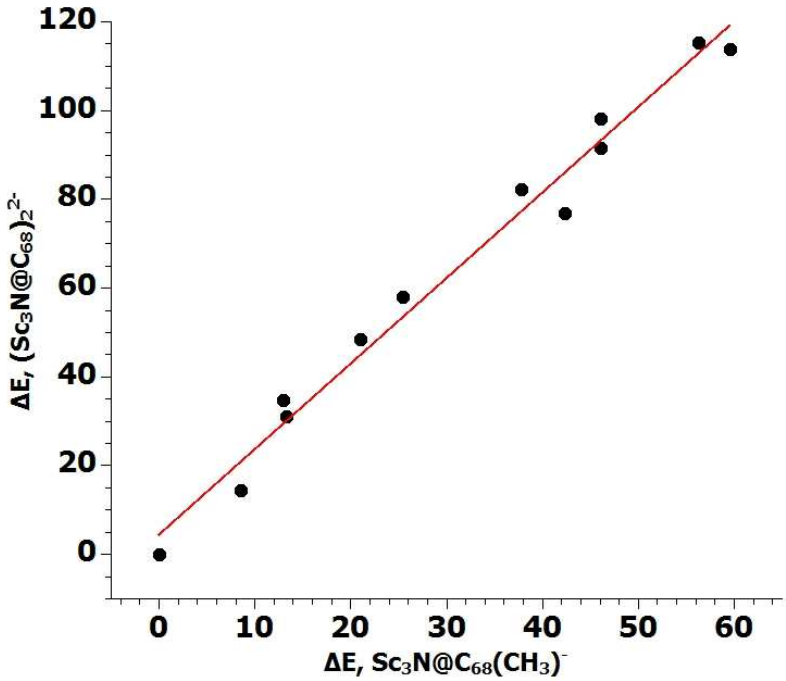
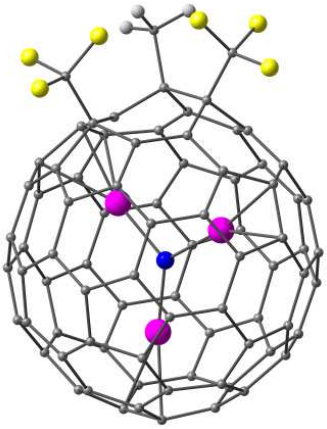


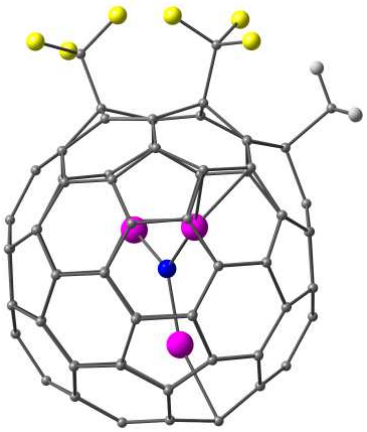
Figure S1. Correlation between relative energies of $Sc_3N@C_{68}(CH_3)^-$ and $(Sc_3N@C_{68})_2^{2-}$.
$\Delta E(\text{dim}) = 1.93 * \Delta E(CH_3) + 4.5$; $R^2 = 0.982$

Stability of $Sc_3N@C_{80}(CF_3)_2(CH_3)^-$ and $(Sc_3N@C_{80}(CF_3)_2)_2^{2-}$

	CH_3		dimer		
	ΔE, DZ(P)	gap	ΔE, DZ(P)	gap	ΔE, TZ2P
a	0.0	1.26	n/a	n/a	
b	30.4	0.95	85.8	0.86	
c	36.8	1.01	0.0	0.84	10.1
d	38.8	1.21	5.5	1.10	17.0
e	38.9	1.12	5.3	1.02	0.0
f	50.8	1.09	27.5	0.91	
g	55.3	0.97	42.2	0.85	
h	56.4	0.78	57.2	0.62	
i	56.5	0.59	42.2	0.38	
j	57.4	0.74	46.3	0.53	
k	58.1	0.90	45.2	0.69	



a



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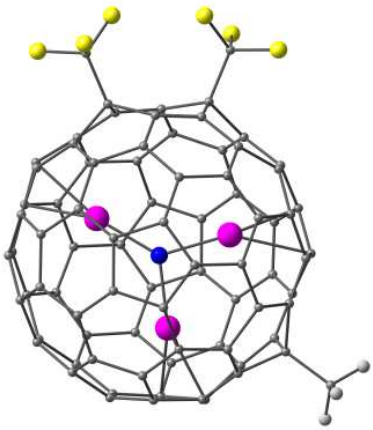

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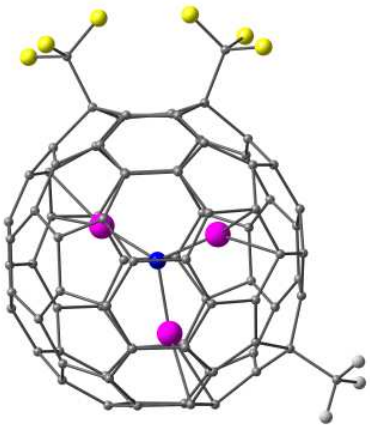

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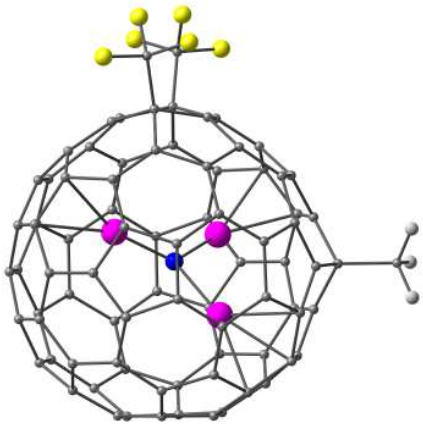
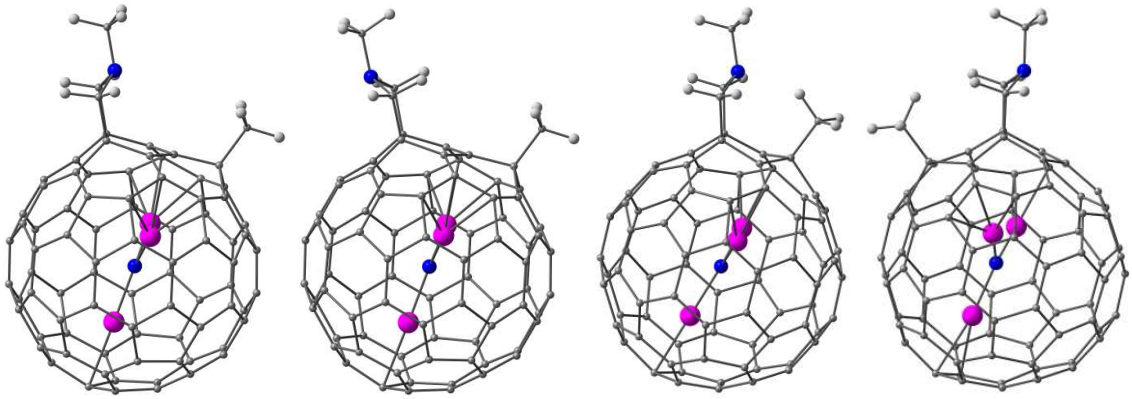


e

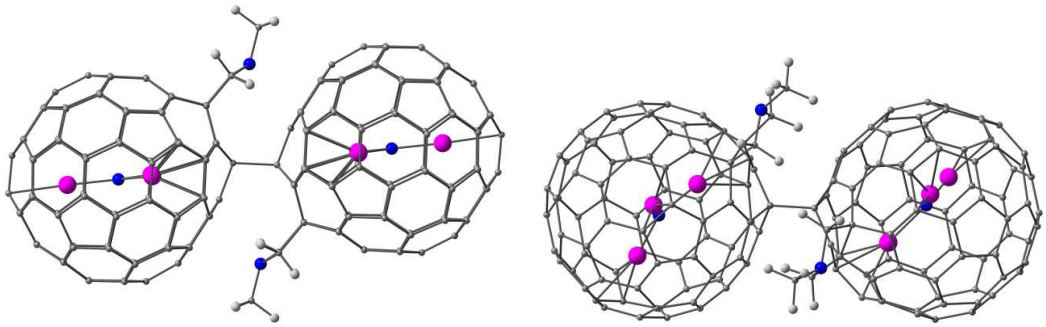
S3. Stability of [5,6]-$Sc_3N@C_{80}(C_3H_7N)(CH_3)^-$ and $([5,6]\text{-}Sc_3N@C_{80}(C_3H_7N))_2^{2-}$

	CH_3		dimer	
	ΔE, DZ(P)	gap	ΔE, DZ(P)	gap
a	0.0	1.33	0.0	1.13
a'	6.9	1.33	9.3	1.13
b	2.9	1.51	146.3	1.38
b'	20.0	1.50	n/a	n/a
c	12.8	1.24	105.7	0.98
d	21.7	0.88	67.9	0.69
e	23.8	1.11	67.3	1.01
f	32.6	0.70	108.9	0.53
g	36.9	0.45	107.3	0.26
h	42.1	0.70	88.2	1.13
i	42.8	0.78	107.7	0.61
j	44.0	0.70	109.0	0.53

The difference between **a/a'** and **b/b'** is in inversion of the pyrrolidine cycle



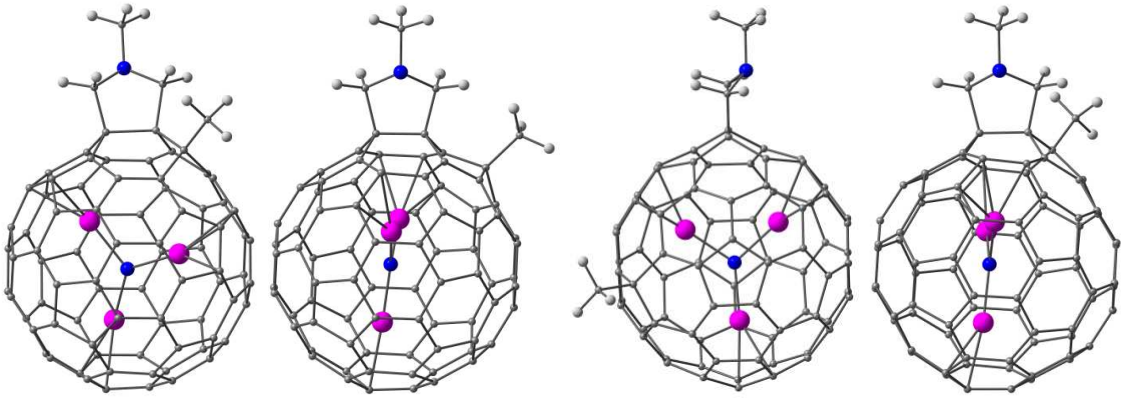
a **a'** **b** **c**



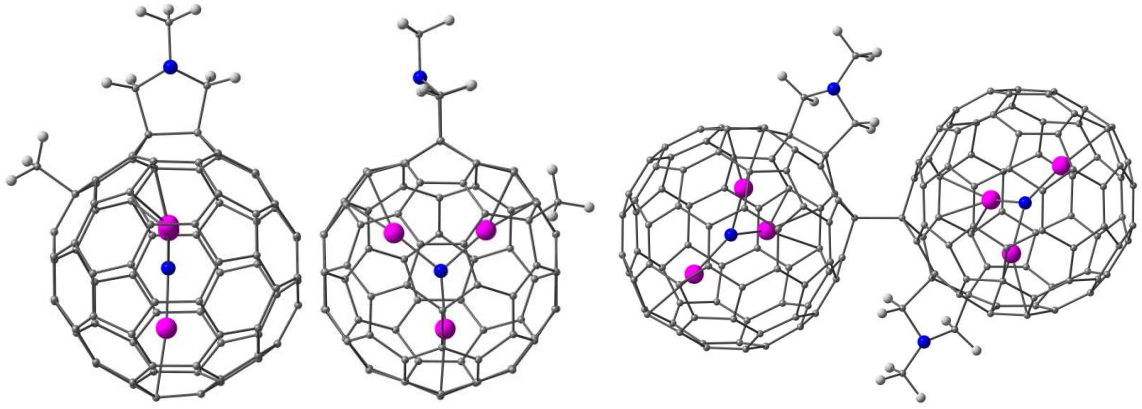
dimer based on **b** dimer based on **c**

S4. Stability of [6,6]-$Sc_3N@C_{80}(C_3H_7N)(CH_3)^-$ and $([6,6]\text{-}Sc_3N@C_{80}(C_3H_7N))_2^{2-}$

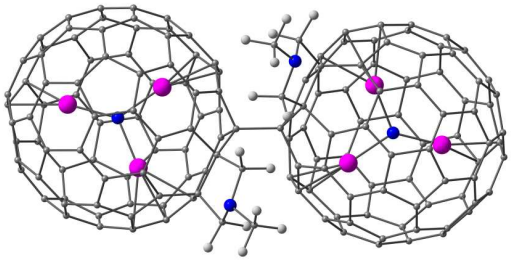
	CH_3		dimer	
	ΔE, DZ(P)	gap	ΔE, DZ(P)	gap
a	0.0	1.34	22.4	1.29
b	6.4	0.87	20.6	0.70
c	23.2	0.67	0.0	0.43
d	25.9	0.60	n/a	n/a
e	27.9	0.64	3.9	0.44
f	31.1	0.72	18.2	0.47



a **b** **c** **d**

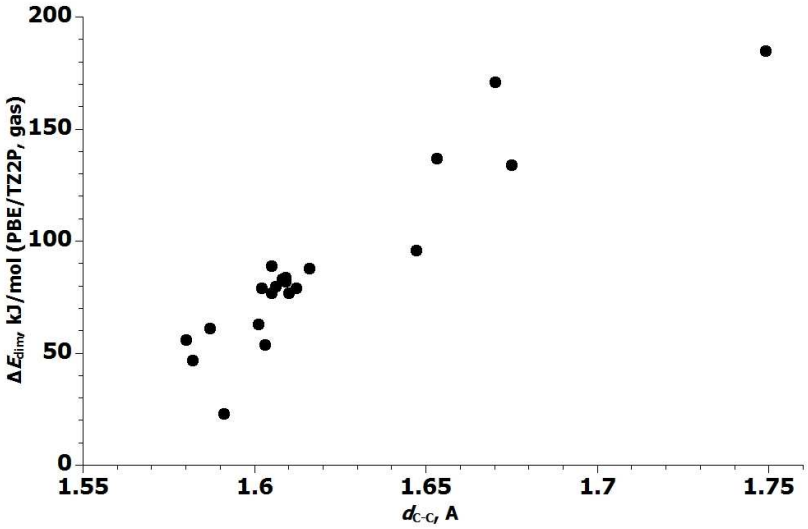


e **f** dimer based on **b**



dimer based on **a**

S5. Correlation between inter-cage bond length and dimerization energy



S6. Components of inter-monomer Coulomb repulsion energy (E_{Coul}, kJ/mol) in NCF dimers

	total	cage-cage	cluster-cage	cluster-cluster
C_{60}	114.7	114.7		
C_{70}	103.1	103.1		
C_{84}-I	96.3	96.3		
C_{84}-II	96.3	96.3		
$Sc_3N@C_{68}$	122.2	348.5	-284.7	58.4
$Sc_3N@C_{80}$	108.2	384.9	-362.9	86.1
$Sc_3N@C_{80}(CF_3)_2$-I	105.0	378.1	-359.8	86.6
$Sc_3N@C_{80}(CF_3)_2$-II	103.4	363.2	-340.3	80.5
[5,6] $Sc_3N@C_{80}(C_3H_7N)$	107.7	391.1	-373.2	89.8
[6,6] $Sc_3N@C_{80}(C_3H_7N)$-I	107.7	376.8	-351.3	82.2
[6,6] $Sc_3N@C_{80}(C_3H_7N)$-II	103.9	379.7	-363.3	87.4
$Y_3N@C_{78}$	113.3	412.1	-392.5	93.7
$Y_3N@C_{80}$-I	116.3	456.3	-452.6	112.7
$Y_3N@C_{80}$-II	114.5	432.3	-420.8	103.0
[5,6] $Y_3N@C_{80}(C_3H_7N)$	112.6	410.8	-392.4	94.3
[6,6] $Y_3N@C_{80}(C_3H_7N)$-I	116.4	441.9	-431.0	105.5
[6,6] $Y_3N@C_{80}(C_3H_7N)$-II	115.3	445.2	-438.1	108.2
$Y_3N@C_{84}$	109.1	452.3	-460.9	117.7
$Y_3N@C_{86}$-I	112.9	505.1	-533.3	141.0
$Y_3N@C_{86}$-II	108.6	486.1	-513.4	135.9
$Y_3N@C_{86}$-III	114.6	520.8	-553.5	147.3
$Y_3N@C_{86}$-IV	111.5	508.9	-541.9	144.6
$Y_3N@C_{88}$-I	107.4	494.9	-529.6	142.0
$Y_3N@C_{88}$-II	109.7	517.6	-559.6	151.6

S7. ΔE_{solv} values (kJ/mol) for dimerization of fullerene anion-radicals computed in oDCB and CH_2Cl_2 using COSMO-RS model at the PBE/STO-DZVP level

	oDCB	CH_2Cl_2
C_{60}	-135.1	-132.5
C_{70}	-126.3	-123.9
C_{84}-I	-121.2	-117.6
C_{84}-II	-119.0	-115.3
$Sc_3N@C_{68}$	-123.1	-121.7
$Sc_3N@C_{80}$	-112.1	-112.5
$Sc_3N@C_{80}(CF_3)_2$-I	-99.9	-94.2
$Sc_3N@C_{80}(CF_3)_2$-II	-102.1	-111.6
[5,6] $Sc_3N@C_{80}(C_3H_7N)$	-80.0	-86.0
[6,6] $Sc_3N@C_{80}(C_3H_7N)$-I	-89.2	-89.5
[6,6] $Sc_3N@C_{80}(C_3H_7N)$-II	-113.4	-112.5
$Y_3N@C_{78}$	-123.3	-119.2
$Y_3N@C_{80}$-I	-130.0	-141.1
$Y_3N@C_{80}$-II	-120.9	-118.6
[5,6] $Y_3N@C_{80}(C_3H_7N)$	-117.1	-113.6
[6,6] $Y_3N@C_{80}(C_3H_7N)$-I	-112.5	-108.1
[6,6] $Y_3N@C_{80}(C_3H_7N)$-II	-120.9	-115.5
$Y_3N@C_{84}$	-124.7	-122.6
$Y_3N@C_{86}$-I	-130.8	-127.2
$Y_3N@C_{86}$-II	-111.0	-113.7
$Y_3N@C_{86}$-III	-117.6	-104.7
$Y_3N@C_{86}$-IV	-123.4	-103.6
$Y_3N@C_{88}$-I	-84.1	-83.3
$Y_3N@C_{88}$-II	-126.5	-124.0