Supporting Information

Metal Atoms Collinear with the Spiro Carbon of 6,6-Open Adducts, $M_2@C_{80}(Ad)$ (M = La and Ce, Ad = adamantylidene)

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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. GAUSSIAN 03, Revision C. 01, Gaussian Inc., Wallingford, CT, 2004.

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Maeda, Y.; Matsunaga, Y.; Wakahara, T.; Takahashi, S.; Tsuchiya, T.; Ishitsuka, M. O.; Hasegawa, T.; Akasaka, T.; Liu, M. T. H.; Kokura, K.; Horn, E.; Yoza, K.; Kato, T.; Okubo, S.; Kobayashi, K.; Nagase, S.; Yamamoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 6858–6859.

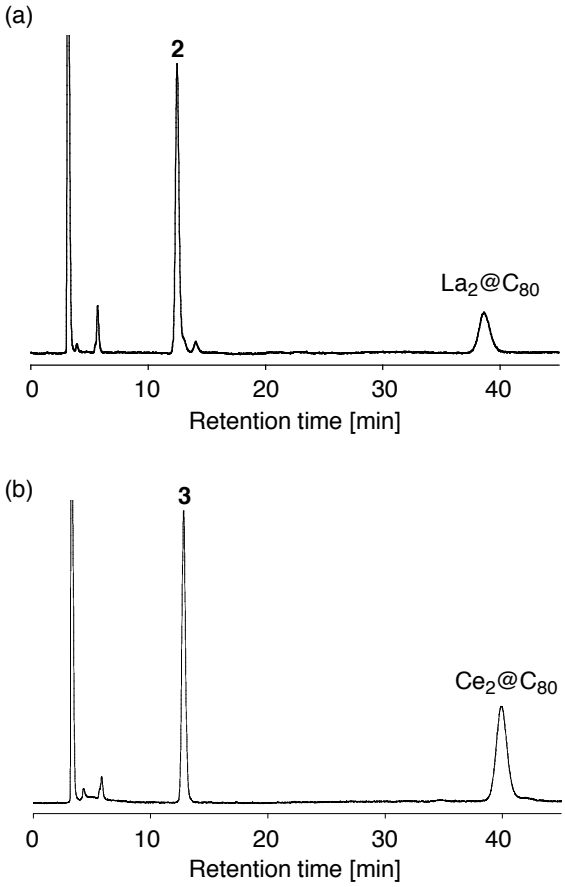

Figure S1. HPLC profiles of the reaction mixtures for photochemical reactions of (a) $La_2@C_{80}$ with **1** and (b) $Ce_2@C_{80}$ with **1**. Conditions: column, Buckyprep (4.6 mm × 250 mm i.d.); eluent, toluene 1.0 mL/min.

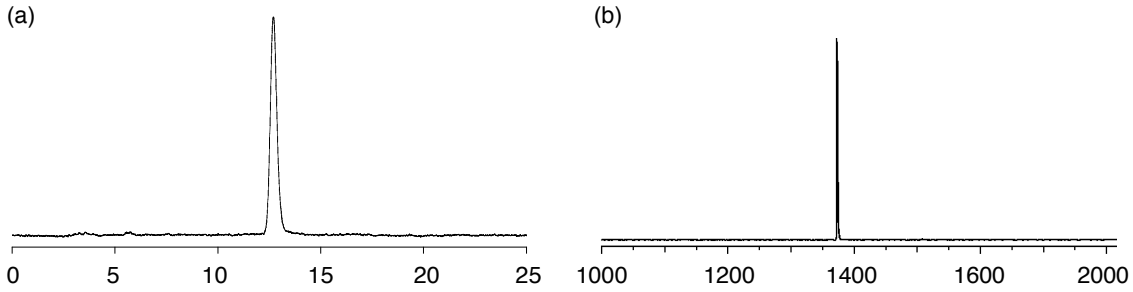

Figure S2. (a) HPLC profiles of **2**. Conditions: column, Buckyprep (4.6 mm × 250 mm i.d.); eluent, toluene 1.0 mL/min. (b) MALDI-TOF mass spectrum of **2**.

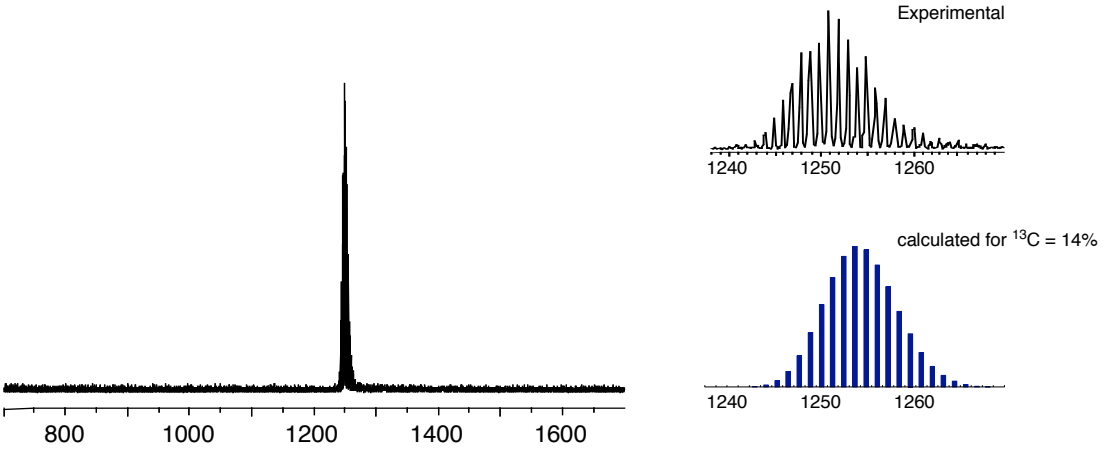

Figure S3. MALDI-TOF mass spectrum of ^{13}C –enriched $Ce_2@C_{80}$.

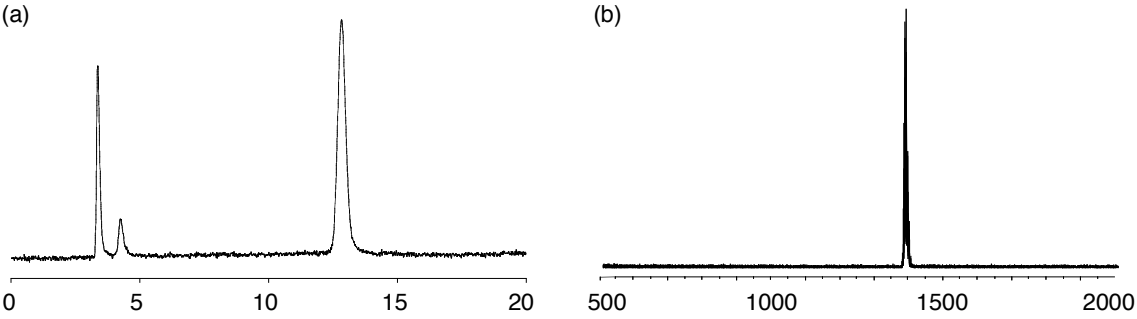

Figure S4. (a) HPLC profiles of ^{13}C-eniched **3**. Conditions: column, Buckyprep (4.6 mm × 250 mm i.d.); eluent, toluene 1.0 mL/min. (b) MALDI-TOF mass spectrum of ^{13}C-enriched **2**.

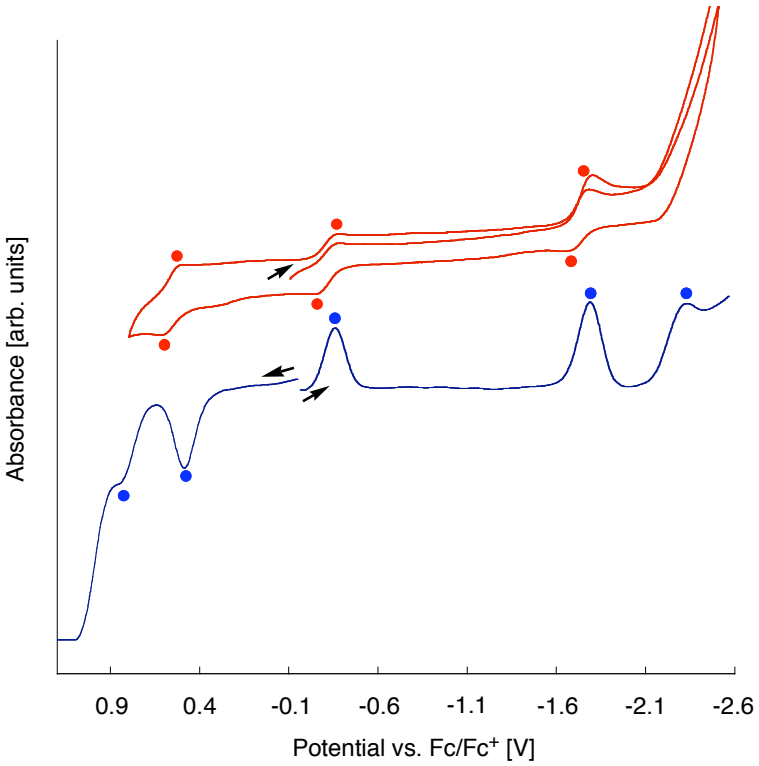

Figure S5. Cyclic and differential pulse voltammogram of **2**.

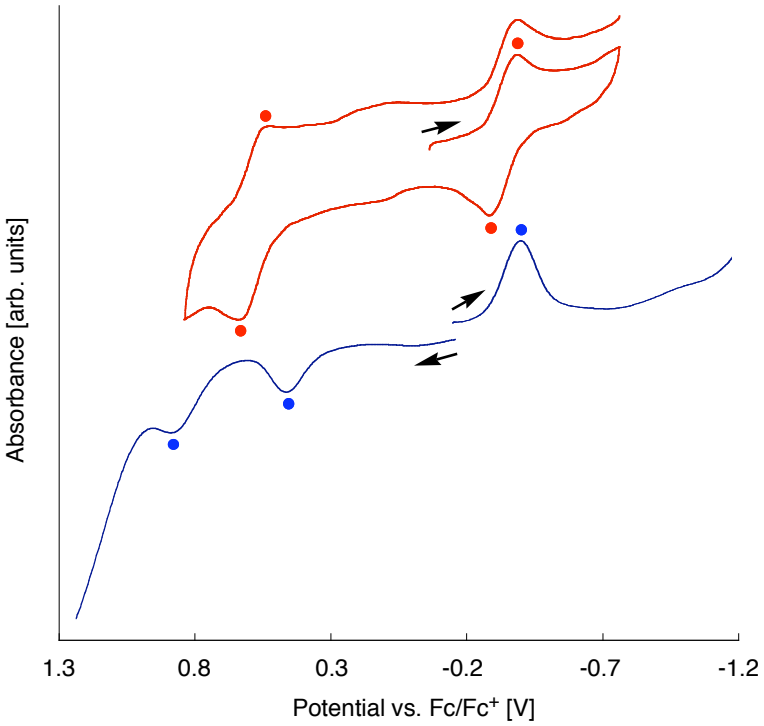

Figure S6. Cyclic and differential pulse voltammogram of **3**.

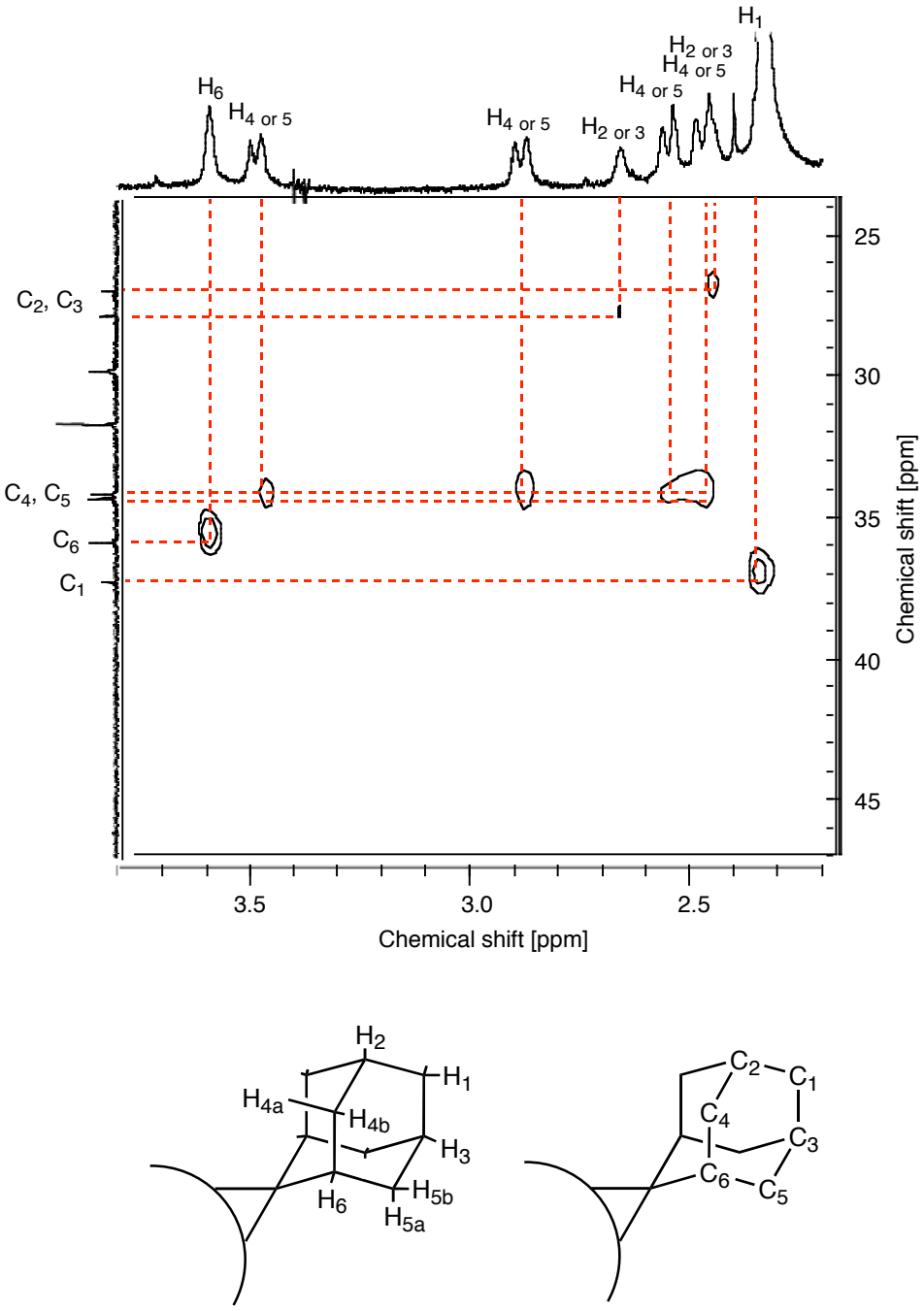

Figure S7. HMQC NMR spectrum of **2** in $C_2D_2Cl_4/CS_2$ at 303 K.

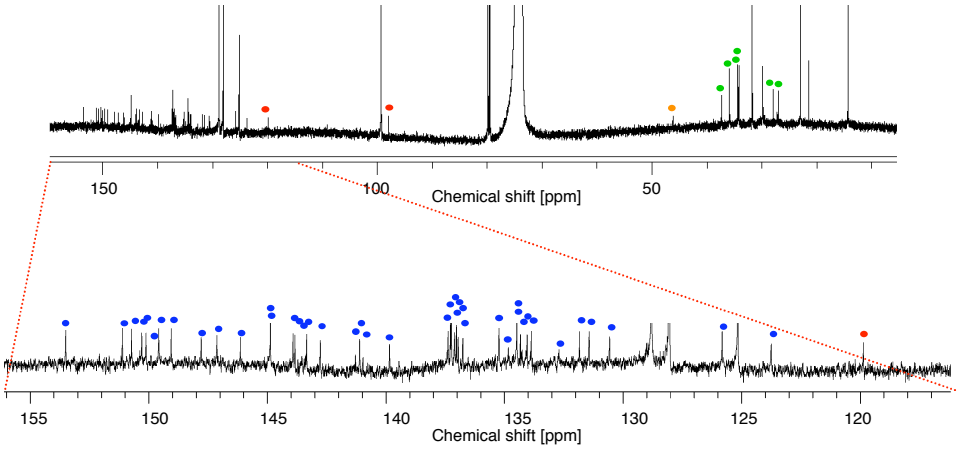

Figure S8. ^{13}C NMR spectrum of **2** in $C_2D_2Cl_4/CS_2$ at 303 K. The signals marked by blue, red, orange and green solid circles are due to the sp^2-carbon atoms on the cage, sp^2-carbon atoms on the addition position of the cage, spiro carbon on the Ad group, and the other carbon atoms on the Ad group, respectively.

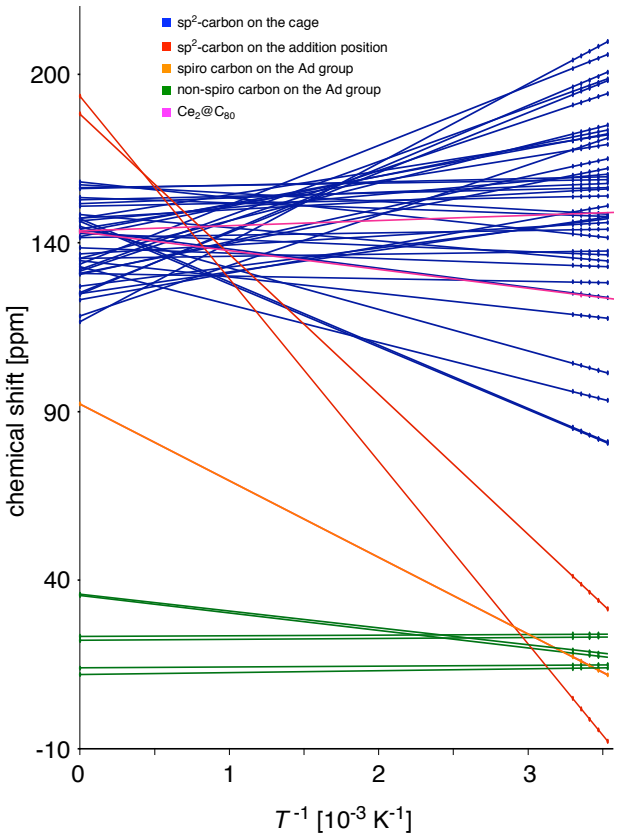

Figure S9. Line-fitting plot; chemical shift vs. T^{-1} of **3**.

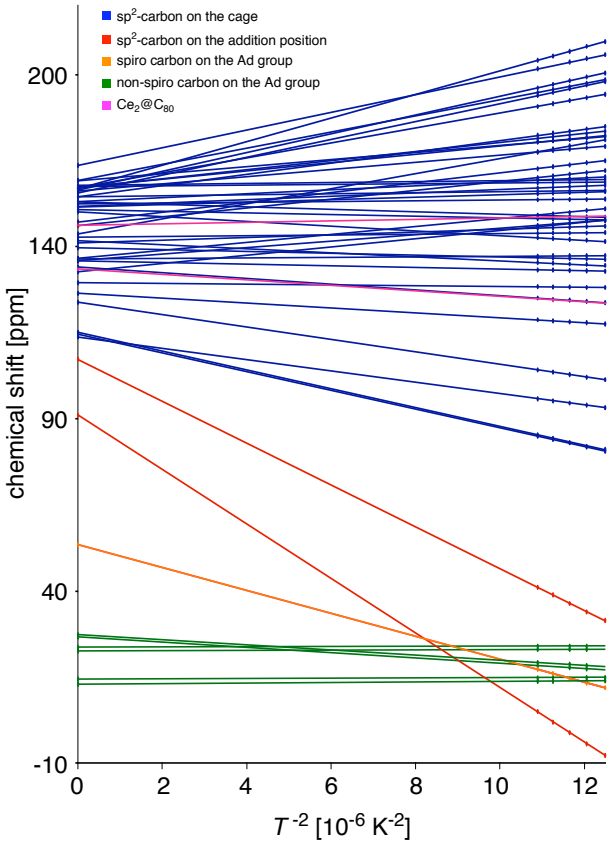

Figure S10. Line-fitting plot; chemical shift vs. T^{-2} of **3**.

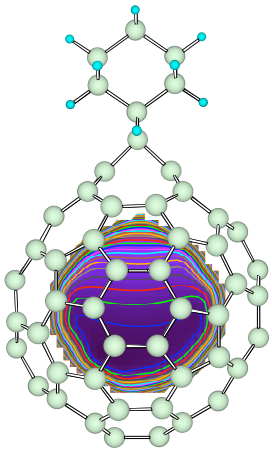

Figure S11. The electrostatic potential map of $[C_{80}(Ad)]^{6-}$.

Table S1. Summary of Crystallographic Data of **2** at 103, 133, 188, and 273 K

Temperature	103 K	133 K	188 K	273 K
Formula	$C_{96}H_{18}Cl_2La_2$	$C_{96}H_{18}Cl_2La_2$	$C_{96}H_{18}Cl_2La_2$	$C_{96}H_{18}Cl_2La_2$
formula weight	1519.82	1519.82	1519.82	1519.82
wavelength, Å	0.71075	0.71075	0.71075	0.71075
crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*
a , Å	21.944(3)	21.958(3)	21.966(3)	22.031(3)
b , Å	22.017(2)	22.035(2)	22.066(3)	22.122(3)
c , Å	20.452(2)	20.4625(17)	20.473(2)	20.498(2)
α , deg	90.00	90.00	90.00	90.00
β , deg	90.00	90.00	90.00	90.00
γ , deg	90.00	90.00	90.00	90.00
Volume, Å^3	9881(2)	9900.8(17)	9924(2)	9990(2)
Z	8	8	8	8
D_{calc}, Mg/m^3	2.043	2.039	2.035	2.021
Absorption coefficient	1.884	1.880	1.876	1.864
F (000)	5936	5936	5936	5936
θ range, deg	3.09 to 27.49	3.09 to 27.42	3.09 to 27.48	3.08 to 27.48
Limiting indices	-28 <= h <= 28	-28 <= h <= 28	-28 <= h <= 28	-27 <= h <= 28
	-23 <= k <= 28	-24 <= k <= 28	-23 <= k <= 28	-24 <= k <= 28
	-25 <= l <= 26	-26 <= l <= 26	-25 <= l <= 26	-26 <= l <= 26
Reflections collected	77189	89327	77851	67464
Independent reflections	11216	11244	11266	11273
data / restraints / parameters	11216 / 834 / 909	11244 / 834 / 909	11266 / 834 / 909	11273 / 834 / 901
R_{int}	0.0784	0.0796	0.0783	0.0858
R_1 [$I > 2\sigma(I)$]	0.0602	0.0590	0.0593	0.0746
wR_2 [$I > 2\sigma(I)$]	0.1631	0.1609	0.1582	0.1800
R_1 [all data]	0.0806	0.0757	0.0843	0.1178
wR_2 [all data]	0.1714	0.1680	0.1675	0.1945
GOF on F^2	1.218	1.232	1.148	1.192
max, min peaks, e/Å^3	3.904, -1.304	3.918, -1.220	2.086, -1.407	3.559, -0.894

Table S2 Total Energies (Hartree) and Cartesian Coordinates (Å) of $La_2@C_{80}(Ad)$

Structure **a**

Total energy = -3500.43798213

La -0.005210 1.220627 0.000000

La 0.018793 -2.684743 0.000000

C 3.292665 1.072103 1.446665

C 2.660931 0.735452 2.670578

C 2.646974 -0.618950 3.133972

C 1.414880 -0.824091 3.849761

C 0.739216 -2.078949 3.804767

C 3.977643 0.059428 0.720363

C 3.943807 -1.301504 1.167690

C 3.239084 -1.660724 2.351998

C 2.597752 -2.944976 2.365747

C 1.368080 -3.150894 3.080716

C 3.926406 -2.151183 0.000000

C 3.227866 -3.387808 0.000000

C 2.605509 -3.810400 1.223350

C -3.281798 -2.807758 1.460741

C -2.673941 -2.442874 2.696998

C 1.433027 1.393426 3.085301

C -1.450978 -3.075259 3.141676

C -2.658251 -1.081357 3.142229

C 0.673144 0.405601 3.816168

C -0.682782 -2.079659 3.856003

C -1.423789 -0.851152 3.851011

C -0.743867 0.403125 3.766742

C 2.714747 2.158262 0.717711

C -2.660236 -3.875843 0.718338

C -3.968145 -1.801696 0.722621

C 1.607837 2.958767 1.189190

C -1.483491 -4.570003 1.178055

C -3.950538 -0.436709 1.167574
C 0.834324 2.474762 2.352777
C -0.825590 -4.108365 2.388454
C -3.245113 -0.058166 2.345366
C -0.636886 2.531166 2.362995
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C -1.364847 1.468567 3.030188
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H -1.248194 7.125987 2.162633
H 0.036266 8.942980 0.882201
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C 2.660931 0.735452 -2.670578
C 2.646974 -0.618950 -3.133972
C 1.414880 -0.824091 -3.849761
C 0.739216 -2.078949 -3.804767
C 3.977643 0.059428 -0.720363
C 3.943807 -1.301504 -1.167690
C 3.239084 -1.660724 -2.351998
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H -1.248194 7.125987 -2.162633
H 0.036266 8.942980 -0.882201

Structure **b**
Total energy = -3500.40264465
La -0.003530 -0.795828 1.846157
La -0.003530 -0.795828 -1.846157
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C 2.624568 -0.638532 3.143287
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C 0.765488 -2.130862 3.937068
C 3.957072 0.046829 0.716808
C 3.931684 -1.320544 1.167118
C 3.235161 -1.686852 2.353999
C 2.603058 -2.962410 2.387848
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C -3.281867 -2.765007 1.445455
C -2.640657 -2.385461 2.682241
C 1.432817 1.380808 3.100558

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C 1.286607 6.495114 -1.250936
C -1.235497 6.480594 -1.252318
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H 1.293246 7.107902 -2.162311
H 2.194352 5.878700 -1.274809
H -2.136378 5.854021 -1.278314
H -1.248789 7.094892 -2.162558
H 0.010304 8.929100 -0.882440

Structure **c**

Total energy = -3500.29013654

La	1.7750000	-2.7500000	0.0000000
La	-1.8580000	-2.7500000	0.0000000
C	3.2270000	-0.9530000	1.4190000
C	2.5980000	-1.3110000	2.6470000
C	2.6020000	-2.6580000	3.1250000
C	1.4350000	-2.8570000	3.9360000
C	0.7630000	-4.1420000	3.9090000

C	3.9020000	-1.9620000	0.7020000
C	3.8850000	-3.3220000	1.1520000
C	3.2030000	-3.6910000	2.3310000
C	2.5840000	-4.9560000	2.3650000
C	1.3560000	-5.1500000	3.0970000
C	3.8650000	-4.1580000	0.0000000
C	3.1650000	-5.3840000	0.0000000
C	2.5590000	-5.7890000	1.2090000
C	-3.2480000	-4.7620000	1.4290000
C	-2.6180000	-4.3880000	2.6600000
C	1.4290000	-0.6520000	3.1040000
C	-1.4340000	-5.0330000	3.1250000
C	-2.6220000	-3.0490000	3.1310000
C	0.6810000	-1.5810000	3.9360000
C	-0.6850000	-4.1040000	3.9310000
C	-1.4390000	-2.8310000	3.9440000
C	-0.7730000	-1.5400000	3.9350000
C	2.6640000	0.1150000	0.7090000
C	-2.6770000	-5.8280000	0.7060000
C	-3.9160000	-3.7560000	0.7080000
C	1.5210000	0.8280000	1.1730000
C	-1.4770000	-6.4690000	1.1520000
C	-3.8950000	-2.3950000	1.1540000
C	0.8420000	0.4040000	2.3160000
C	-0.8220000	-6.0560000	2.3320000
C	-3.2180000	-2.0250000	2.3310000
C	-0.5990000	0.4560000	2.3360000
C	0.5860000	-6.1250000	2.3640000
C	-2.5750000	-0.7650000	2.3500000
C	-1.3510000	-0.5530000	3.0820000
C	0.8900000	1.4520000	0.0000000
C	-0.7360000	-6.8560000	0.0000000
C	-3.8790000	-1.5540000	0.0000000

C	-0.8240000	1.4330000	0.0000000
C	0.6750000	-6.8390000	0.0000000
C	-3.1770000	-0.3390000	0.0000000
C	-1.3510000	0.8290000	1.2180000
C	1.3260000	-6.5100000	1.2090000
C	-2.5550000	0.0630000	1.2050000
C	0.0210000	2.6770000	0.0000000
C	0.0200000	3.5460000	1.2530000
C	1.2740000	4.4420000	1.2440000
C	1.2680000	5.3370000	0.0000000
C	-1.2540000	5.3190000	0.0000000
C	-1.2460000	4.4250000	1.2460000
C	0.0010000	6.2150000	0.0000000
H	0.0230000	2.9320000	2.1410000
H	1.2780000	5.0540000	2.1410000
H	2.1690000	3.8270000	1.2600000
H	2.1500000	5.9680000	0.0000000
H	-2.1450000	5.9370000	0.0000000
H	-2.1320000	3.7980000	1.2650000
H	-1.2580000	5.0380000	2.1410000
H	-0.0040000	6.8560000	0.8690000
C	3.2270000	-0.9530000	-1.4190000
C	2.5980000	-1.3110000	-2.6470000
C	2.6020000	-2.6580000	-3.1250000
C	1.4350000	-2.8570000	-3.9360000
C	0.7630000	-4.1420000	-3.9090000
C	3.9020000	-1.9620000	-0.7020000
C	3.8850000	-3.3220000	-1.1520000
C	3.2030000	-3.6910000	-2.3310000
C	2.5840000	-4.9560000	-2.3650000
C	1.3560000	-5.1500000	-3.0970000
C	2.5590000	-5.7890000	-1.2090000
C	-3.2480000	-4.7620000	-1.4290000

C	-2.6180000	-4.3880000	-2.6600000
C	1.4290000	-0.6520000	-3.1040000
C	-1.4340000	-5.0330000	-3.1250000
C	-2.6220000	-3.0490000	-3.1310000
C	0.6810000	-1.5810000	-3.9360000
C	-0.6850000	-4.1040000	-3.9310000
C	-1.4390000	-2.8310000	-3.9440000
C	-0.7730000	-1.5400000	-3.9350000
C	2.6640000	0.1150000	-0.7090000
C	-2.6770000	-5.8280000	-0.7060000
C	-3.9160000	-3.7560000	-0.7080000
C	1.5210000	0.8280000	-1.1730000
C	-1.4770000	-6.4690000	-1.1520000
C	-3.8950000	-2.3950000	-1.1540000
C	0.8420000	0.4040000	-2.3160000
C	-0.8220000	-6.0560000	-2.3320000
C	-3.2180000	-2.0250000	-2.3310000
C	-0.5990000	0.4560000	-2.3360000
C	0.5860000	-6.1250000	-2.3640000
C	-2.5750000	-0.7650000	-2.3500000
C	-1.3510000	-0.5530000	-3.0820000
C	-1.3510000	0.8290000	-1.2180000
C	1.3260000	-6.5100000	-1.2090000
C	-2.5550000	0.0630000	-1.2050000
C	0.0200000	3.5460000	-1.2530000
C	1.2740000	4.4420000	-1.2440000
C	-1.2460000	4.4250000	-1.2460000
H	0.0230000	2.9320000	-2.1410000
H	1.2780000	5.0540000	-2.1410000
H	2.1690000	3.8270000	-1.2600000
H	-2.1320000	3.7980000	-1.2650000
H	-1.2580000	5.0380000	-2.1410000
H	-0.0040000	6.8560000	-0.8690000