

## Electronic Supplementary Materials for: Photoinduced Relaxation

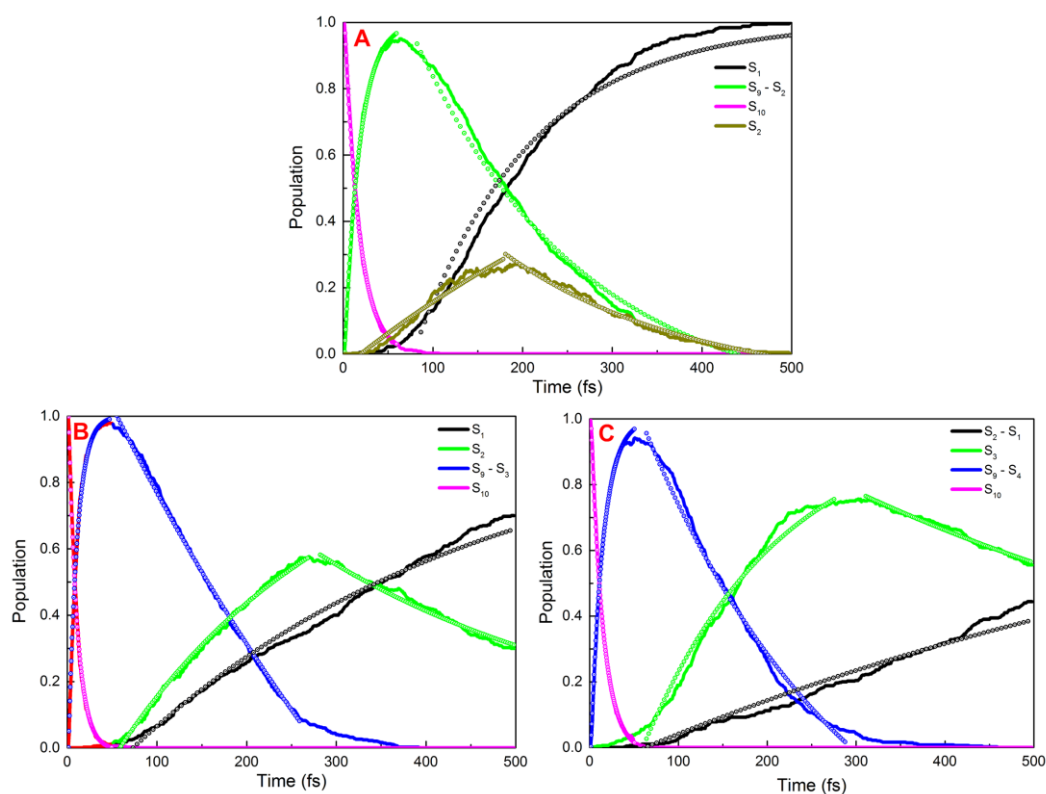
### **Dynamics of Nitrogen-Capped Silicon Nanoclusters: a TD-DFT Study**

Xiang-Yang Liu, Xiao-Ying Xie, Wei-Hai Fang, and Ganglong Cui\*

Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China

Email: [ganglong.cui@bnu.edu.cn](mailto:ganglong.cui@bnu.edu.cn)

#### 1. Time-Dependent State Populations and Related Fitting Lines



**Fig. S1:** Time-dependent state populations of (A) Cl@SiQD, (B) Car@SiQD, and (C) Azo@SiQD upon irradiation to the outset of their characteristic absorption band i.e. the  $S_{10}$  state (solid lines) and their related fitting lines (dot lines).

## 2. Vertical Excitation Transitions of Silicon Nanoclusters

**Table S1:** TD-CAM-B3LYP Computed Energies (eV/nm), Oscillator Strengths, and Electronic Configurations of the Lowest 10 Electronic Excitations of Cl@SiQD.

	MO (weight %)	Energy (eV/nm)	Osc.
$S_0 \rightarrow S_1$	HOMO $\rightarrow$ LUMO (67)	4.82 (257)	0.0037
$S_0 \rightarrow S_2$	HOMO-1 $\rightarrow$ LUMO (47) HOMO-3 $\rightarrow$ LUMO (17) HOMO-6 $\rightarrow$ LUMO (11)	4.96 (250)	0.0065
$S_0 \rightarrow S_3$	HOMO-2 $\rightarrow$ LUMO (67)	5.09 (243)	0.0008
$S_0 \rightarrow S_4$	HOMO-1 $\rightarrow$ LUMO (23) HOMO $\rightarrow$ LUMO+3 (23)	5.12 (242)	0.0001
$S_0 \rightarrow S_5$	HOMO-1 $\rightarrow$ LUMO+1 (37) HOMO-1 $\rightarrow$ LUMO+2 (32)	5.16 (241)	0.0004
$S_0 \rightarrow S_6$	HOMO-5 $\rightarrow$ LUMO (9) HOMO $\rightarrow$ LUMO+1 (32) HOMO $\rightarrow$ LUMO+2 (11)	5.16 (240)	0.0012
$S_0 \rightarrow S_7$	HOMO-2 $\rightarrow$ LUMO+1 (30) HOMO-2 $\rightarrow$ LUMO+2 (14) HOMO-1 $\rightarrow$ LUMO+3 (17)	5.17 (240)	0.0011
$S_0 \rightarrow S_8$	HOMO-1 $\rightarrow$ LUMO+1 (13) HOMO-1 $\rightarrow$ LUMO+2 (27) HOMO-1 $\rightarrow$ LUMO+3 (16)	5.17 (240)	0.0000
$S_0 \rightarrow S_9$	HOMO-2 $\rightarrow$ LUMO+3 (31) HOMO-1 $\rightarrow$ LUMO+3 (17)	5.18 (239)	0.0002
$S_0 \rightarrow S_{10}$	HOMO-5 $\rightarrow$ LUMO (25) HOMO $\rightarrow$ LUMO+2 (29)	5.19 (239)	0.0035

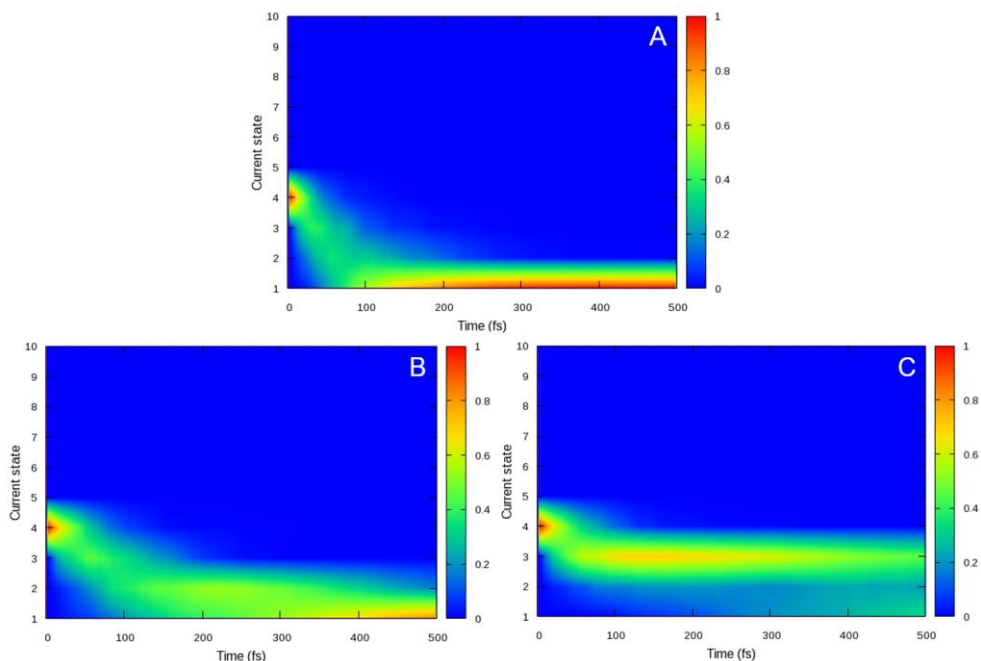
**Table S2:** TD-CAM-B3LYP Computed Energies (eV/nm), Oscillator Strengths, and Electronic Configurations of the Lowest 10 Electronic Excitations of Car@SiQD.

	MO (weight %)	Energy (eV/nm)	Osc.
$S_0 \rightarrow S_1$	HOMO $\rightarrow$ LUMO (61) HOMO $\rightarrow$ LUMO+6 (11)	4.32 (287)	0.0204
$S_0 \rightarrow S_2$	HOMO $\rightarrow$ LUMO+1 (15) HOMO $\rightarrow$ LUMO+7 (19) HOMO $\rightarrow$ LUMO+8 (10) HOMO $\rightarrow$ LUMO+11 (12) HOMO $\rightarrow$ LUMO+19 (12)	4.46 (278)	0.1222
$S_0 \rightarrow S_3$	HOMO $\rightarrow$ LUMO+1 (41) HOMO $\rightarrow$ LUMO+8 (10)	4.64 (267)	0.0185
$S_0 \rightarrow S_4$	HOMO $\rightarrow$ LUMO+2 (16) HOMO $\rightarrow$ LUMO+3 (22)	4.77 (260)	0.0381
$S_0 \rightarrow S_5$	HOMO $\rightarrow$ LUMO+3 (35)	4.82 (257)	0.0424
$S_0 \rightarrow S_6$	HOMO $\rightarrow$ LUMO+2 (35) HOMO $\rightarrow$ LUMO+4 (10)	4.83 (257)	0.0483
$S_0 \rightarrow S_7$	HOMO $\rightarrow$ LUMO+2 (19) HOMO $\rightarrow$ LUMO+4 (48)	4.89 (254)	0.0166
$S_0 \rightarrow S_8$	HOMO $\rightarrow$ LUMO+5 (54)	4.96 (250)	0.0146
$S_0 \rightarrow S_9$	HOMO-1 $\rightarrow$ LUMO (48) HOMO-1 $\rightarrow$ LUMO+1 (15)	4.99 (249)	0.0081
$S_0 \rightarrow S_{10}$	HOMO-3 $\rightarrow$ LUMO (22) HOMO-2 $\rightarrow$ LUMO (46)	5.04 (246)	0.0043

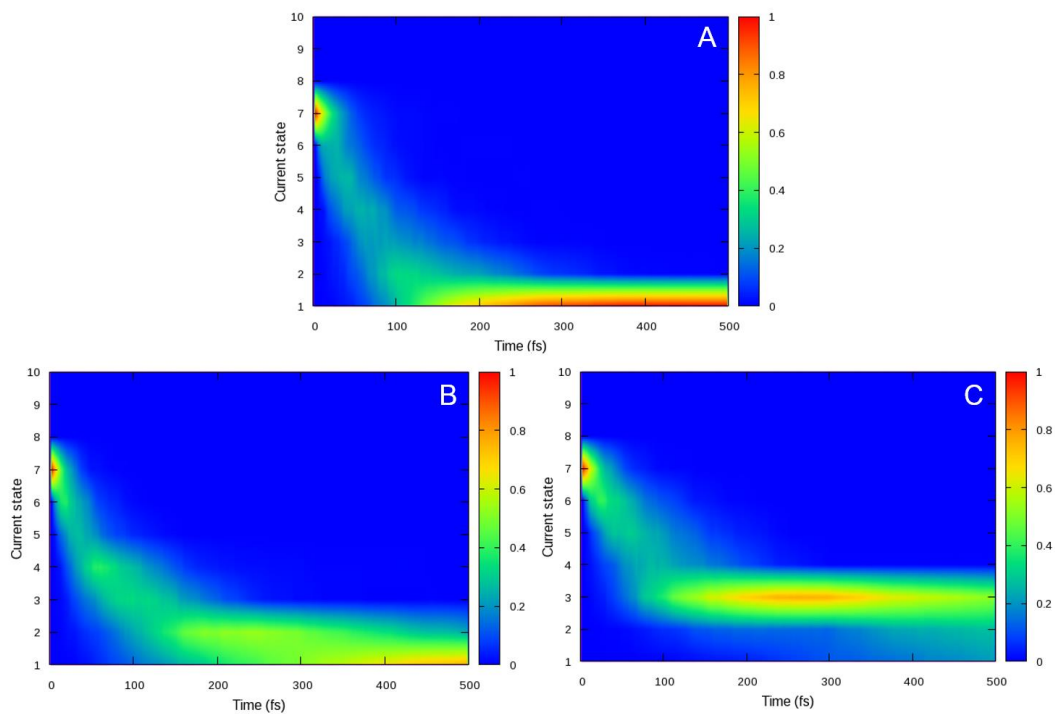
**Table S3:** TD-CAM-B3LYP Computed Energies (eV/nm), Oscillator Strengths, and Electronic Configurations of the Lowest 10 Electronic Excitations of Azo@SiQD.

	MO (weight %)	Energy (eV/nm)	Osc.
$S_0 \rightarrow S_1$	HOMO $\rightarrow$ LUMO (75)	3.17 (391)	0.0425
$S_0 \rightarrow S_2$	HOMO-1 $\rightarrow$ LUMO (83)	3.74 (331)	0.0008
$S_0 \rightarrow S_3$	HOMO $\rightarrow$ LUMO+1 (63)	3.94 (315)	0.0014
$S_0 \rightarrow S_4$	HOMO $\rightarrow$ LUMO+2 (50)	4.17 (297)	0.2452
$S_0 \rightarrow S_5$	HOMO $\rightarrow$ LUMO+5 (20) HOMO $\rightarrow$ LUMO+21 (18) HOMO $\rightarrow$ LUMO+25 (19)	4.27 (290)	0.0060
$S_0 \rightarrow S_6$	HOMO-1 $\rightarrow$ LUMO+1 (82)	4.32 (287)	0.0565
$S_0 \rightarrow S_7$	HOMO $\rightarrow$ LUMO+2 (18) HOMO $\rightarrow$ LUMO+3 (42)	4.40 (282)	0.3714
$S_0 \rightarrow S_8$	HOMO-7 $\rightarrow$ LUMO (12) HOMO-2 $\rightarrow$ LUMO (40) HOMO $\rightarrow$ LUMO (12)	4.50 (276)	0.0036
$S_0 \rightarrow S_9$	HOMO-1 $\rightarrow$ LUMO+2 (75)	4.51 (275)	0.0013
$S_0 \rightarrow S_{10}$	HOMO $\rightarrow$ LUMO+5 (19) HOMO $\rightarrow$ LUMO+21 (10)	4.58 (271)	0.0095

### 3. Evolution of Probability Density of the Current Electronic State



**Fig. S2:** Contour plot of the probability density of the current electronic state of (A) Cl@SiQD, (B) Car@SiQD, and (C) Azo@SiQD during the excited-state relaxation from the initial  $S_4$  to the  $S_1$  state.



**Fig. S3:** Contour plot of the probability density of the current electronic state of (A) Cl@SiQD, (B) Car@SiQD, and (C) Azo@SiQD during the excited-state relaxation from the initial  $S_7$  to the  $S_1$  state.

#### 4. Cartesian Coordinates of All Optimized S<sub>0</sub> Minima

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Si<sub>35</sub>H<sub>35</sub>Cl

Si	-0.1699350000	-0.0002140000	0.0020060000
Si	-0.1549970000	3.8595770000	0.2838830000
Si	1.1506300000	1.6662780000	3.2303040000
Si	-2.6554140000	1.7396920000	2.4008560000
H	-2.8252140000	2.8950580000	3.3376440000
Si	-0.4611050000	1.8378040000	1.4936790000
H	-0.3392380000	5.0019630000	1.2337850000
H	0.9684490000	2.8245890000	4.1609580000
H	3.4285430000	-5.2270190000	1.2735640000
H	5.0030250000	-3.9537880000	-0.0340220000
H	-4.1697130000	-5.0899640000	-0.3981420000
H	2.1998970000	-4.9466040000	-2.1608830000
H	-1.5972180000	-4.8749080000	-2.9882110000
Si	-1.7920160000	-3.7272520000	-2.0472790000
Si	0.7073000000	-1.6034840000	-4.1693340000
Si	2.0274890000	-3.7976730000	-1.2171880000
Si	-0.1675520000	-3.8560140000	-0.3277520000
H	-2.8330030000	-3.3759650000	2.8414410000
H	-0.3553550000	-5.1332370000	0.4302260000
Si	-0.4671290000	-2.0477880000	1.1858230000
H	0.9606620000	-3.4465120000	3.6623370000
H	-1.5318010000	-1.6928170000	6.1125830000
H	2.3609640000	0.4671410000	-5.9606600000
Si	2.2919430000	-1.7726390000	-2.4163760000
Si	2.0236030000	0.0716270000	-0.9410650000
Si	3.6195100000	-3.9509490000	0.5221160000
Si	3.5811960000	-0.0719390000	0.8482910000
H	4.3357580000	-2.1802290000	3.1012040000
Si	1.1456080000	-2.1560000000	2.9266260000
Si	0.8309810000	-0.3514020000	4.4284300000
Si	3.3280770000	-2.1279500000	1.9970800000
Si	3.3327100000	1.7784150000	2.3071730000
H	1.8527190000	-0.4391750000	5.5184250000
H	5.0163780000	3.8871470000	0.5824860000
H	4.3405970000	1.6535550000	3.4053560000
H	-4.9856450000	-3.7422810000	-2.2205800000
H	0.0047720000	0.5106140000	-6.4616680000
Si	-1.4631080000	-1.6992280000	-3.2258260000

H	-4.9512070000	0.1574420000	-1.9128900000
H	-2.4794510000	-1.5982720000	-4.3204080000
H	-2.4744540000	2.2651220000	-4.0136090000
Si	-1.7769770000	0.1418680000	-1.7552540000
Si	-3.9681220000	-3.8038830000	-1.1295340000
Si	-3.9528200000	0.0685880000	-0.8008910000
Si	-2.6612960000	-2.0876280000	2.0986390000
H	-5.6279090000	-2.0135780000	0.9372270000
Si	-4.2526730000	-1.9812390000	0.3473460000
Si	-4.2467570000	1.9143860000	0.6548550000
Si	-2.9305630000	-0.2804170000	3.6064770000
H	-4.3138710000	-0.3225480000	4.1766490000
Si	0.9988930000	0.4217150000	-5.3510500000
H	0.8948770000	3.5287020000	-4.6004010000
Si	2.2975420000	2.1230650000	-2.1085920000
Si	-1.4572670000	2.1897760000	-2.9177730000
Si	-1.7795070000	4.0085050000	-1.4341010000
Si	0.7128940000	2.2373410000	-3.8658850000
Si	2.0398400000	3.9357810000	-0.6053060000
Si	-1.3431090000	-0.4226440000	5.3507100000
H	-1.5291530000	0.7079710000	6.3080320000
H	2.2143720000	5.2186760000	-1.3561520000
Si	3.6336060000	3.8075180000	1.1345500000
H	3.4520120000	4.9524970000	2.0756210000
H	-4.9719610000	4.0500450000	-1.6110560000
H	-5.6222930000	1.8592170000	1.2425310000
H	-1.5805900000	5.2896010000	-2.1820510000
Si	-3.9575980000	3.9434290000	-0.5204940000
H	-4.1632030000	5.1009850000	0.4000580000
H	0.8861020000	-2.7627770000	-5.0991540000
H	3.6691720000	-1.7165000000	-2.9961120000
Cl	5.5408330000	-0.0061900000	0.0243780000
H	3.6745240000	2.1527700000	-2.6905640000
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Si <sub>35</sub> C <sub>12</sub> NH <sub>43</sub>			
Si	-0.9468770000	-0.0133330000	0.0063690000
Si	-2.3540900000	3.3978170000	1.3067390000
Si	-2.0206320000	0.3683330000	3.7182510000
Si	-4.7242310000	0.4110940000	0.9207730000
H	-5.6317390000	1.1261310000	1.8733910000
Si	-2.5016560000	1.0399310000	1.4909110000
H	-3.3467790000	4.0123900000	2.2429470000

H	-2.9638760000	1.0833310000	4.6351430000
H	2.5141540000	-5.0780740000	1.5277940000
H	4.2646760000	-3.4547610000	1.8622320000
H	-2.6193360000	-4.8691330000	-4.0063540000
H	3.2060800000	-3.6464600000	-1.7246150000
H	0.7077320000	-3.4671990000	-4.4204580000
Si	-0.2658160000	-2.7720030000	-3.5209300000
Si	2.4202830000	-2.8546910000	-0.7302190000
Si	0.1915530000	-3.3901340000	-1.2860480000
H	-3.6315230000	-4.4442920000	-0.2257230000
H	0.0870110000	-4.8778670000	-1.1517140000
Si	-1.3003240000	-2.3585860000	0.2177560000
H	-0.9824060000	-4.5024140000	2.5403280000
H	-4.7371650000	-4.0462410000	3.5386470000
H	3.6992420000	3.1213240000	-3.4767270000
Si	2.9029600000	-0.5229750000	-0.9679730000
Si	1.3371910000	0.5897800000	0.5479040000
H	2.6881580000	3.4903620000	0.8404130000
H	3.1020580000	0.2417360000	3.1807160000
Si	2.8389380000	-3.6208400000	1.4718340000
Si	1.7010900000	-0.1101410000	2.7926200000
H	1.7178610000	-2.8816740000	4.3661450000
Si	-0.8199560000	-3.0170710000	2.4483110000
Si	-2.3399660000	-1.9679420000	3.9268210000
Si	1.4216590000	-2.4593120000	2.9609090000
Si	0.1987920000	0.9949680000	4.2597200000
H	-2.0296450000	-2.3866040000	5.3299100000
H	1.7807730000	3.7801300000	4.4160290000
H	0.4988690000	0.5583960000	5.6598710000
H	-2.7876050000	-2.9771750000	-5.4882040000
H	1.7176940000	2.8443840000	-4.8059700000
Si	0.0647400000	-0.4337670000	-3.6696710000
H	-3.9777260000	0.4553890000	-4.1531920000
H	-0.2025320000	0.0153810000	-5.0726440000
H	-1.5825980000	3.4267660000	-3.7727950000
Si	-1.4737360000	0.6538610000	-2.2193240000
Si	-2.4751430000	-3.3851170000	-4.0863150000
Si	-3.7059390000	0.0210420000	-2.7463730000
Si	-3.5259780000	-2.9561510000	-0.3508090000
H	-5.3775840000	-2.6846680000	-2.9383870000
Si	-3.9663900000	-2.3259110000	-2.5922740000
Si	-5.2270140000	1.1018610000	-1.2885050000



Si	-5.0243800000	-1.9224850000	1.1595870000
H	-6.4321830000	-2.2825080000	0.8019940000
Si	2.3176280000	2.5642210000	-3.4666980000
H	1.0950140000	5.1062490000	-1.9630890000
Si	1.3606300000	2.9776950000	0.4042190000
Si	-1.2838000000	3.0180650000	-2.3640890000
Si	-2.8382510000	4.0644850000	-0.9133870000
Si	0.9434630000	3.6214330000	-1.8464970000
Si	-0.1601000000	4.0109730000	1.8942660000
Si	-4.5587920000	-2.5717860000	3.3835260000
H	-5.5165240000	-1.9037970000	4.3143560000
H	0.0183160000	5.4910050000	1.7547060000
Si	0.3895920000	3.3445650000	4.0937070000
H	-0.5247670000	3.9935560000	5.0799580000
H	-5.3556230000	3.8742850000	-2.8824740000
H	-6.6160470000	0.6607080000	-1.6299240000
H	-2.6740690000	5.5480050000	-1.0263640000
Si	-5.0435670000	3.4470660000	-1.4861950000
H	-6.0196320000	4.1209790000	-0.5793500000
C	6.8239820000	-0.4785450000	0.2129900000
C	7.9764650000	-1.1830030000	0.5763230000
C	8.0325450000	-2.5544150000	0.3547500000
C	6.9528520000	-3.2062310000	-0.2571080000
C	5.7962090000	-2.5173930000	-0.6220350000
C	5.7067180000	-1.1496400000	-0.3465980000
H	8.8230370000	-0.6565780000	1.0094070000
H	8.9211730000	-3.1159240000	0.6282190000
H	7.0175190000	-4.2694200000	-0.4718100000
H	5.0138240000	-3.0466330000	-1.1448500000
C	6.6969530000	3.3250730000	0.3467460000
C	7.2482940000	2.0658000000	0.5645060000
C	6.5129270000	0.9297410000	0.2124830000
C	5.2146320000	1.0560270000	-0.3365260000
C	4.6806900000	2.3195910000	-0.5789340000
C	5.4259270000	3.4459230000	-0.2325580000
H	7.2580310000	4.2173990000	0.6086810000
H	8.2443600000	1.9638770000	0.9871700000
H	3.7141490000	2.4369460000	-1.0483470000
H	5.0117530000	4.4318310000	-0.4240070000
N	4.6648250000	-0.2179410000	-0.6205970000
Si	2.2990070000	0.2137980000	-3.1583950000
H	3.2124900000	-0.4235030000	-4.1583840000

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Si<sub>35</sub>C<sub>12</sub>N<sub>2</sub>H<sub>44</sub>

Si	1.7802820000	-0.1449370000	-0.0059930000
Si	1.4338250000	1.2684150000	3.4578570000
Si	3.1355180000	3.3840830000	0.6976500000
Si	4.9664350000	0.1018650000	1.7083340000
H	5.9323430000	0.7921140000	2.6118730000
Si	2.8868030000	1.2024450000	1.5637160000
H	2.0613490000	2.1908290000	4.4518990000
H	4.0317440000	4.1376030000	1.6225740000
H	-0.4227300000	1.8152170000	-5.8207380000
H	-2.1214570000	2.9212430000	-4.5276380000
H	3.4896220000	-4.3705830000	-4.1215810000
H	-2.2631960000	-0.7895450000	-4.3736170000
H	-0.1721380000	-4.1666710000	-3.7817740000
Si	0.7151440000	-3.4029450000	-2.8575190000
Si	-1.3865210000	-0.0111770000	-3.4475540000
Si	0.7674700000	-1.1356140000	-3.4864970000
H	5.3674870000	-1.2543900000	-3.3024590000
H	1.1632590000	-1.0523920000	-4.9249870000
Si	2.5232310000	-0.1121530000	-2.2308260000
H	3.4676430000	2.0946260000	-4.2726890000
H	6.9005390000	2.2080160000	-2.5867930000
H	-4.7465370000	-2.2080520000	1.3316670000
Si	-1.9933390000	-0.1129740000	-1.1474750000
Si	-0.1966000000	0.9333200000	-0.1912150000
H	-1.6081190000	3.6258730000	-0.9892610000
Si	-0.9062720000	2.0664260000	-4.4351150000
Si	-0.1923500000	3.1608350000	-0.9637070000
H	0.8862220000	4.5741080000	-3.6126490000
Si	2.7867630000	2.1218920000	-2.9452140000
Si	4.1484210000	3.3064830000	-1.4293060000
Si	0.6922180000	3.1768100000	-3.1287180000
Si	1.0441070000	4.4499790000	0.5458270000
H	4.3226870000	4.7016450000	-1.9288090000
H	-1.4695640000	5.2721900000	2.2648330000
H	1.2353920000	5.8361720000	0.0299800000
H	2.6396340000	-5.8579960000	-2.4383810000
H	-3.2762570000	-4.0550320000	1.8309490000
Si	-0.1862860000	-3.4397650000	-0.7002080000
H	3.2302280000	-4.7481850000	1.4485280000
H	-0.3091210000	-4.8446750000	-0.2105410000

H	0.0341880000	-3.5995020000	3.3861870000
Si	1.2531220000	-2.3106410000	0.7926150000
Si	2.8341750000	-4.4226430000	-2.7850280000
Si	3.3535830000	-3.3472790000	0.9515300000
Si	4.6101420000	-1.1881130000	-2.0187550000
H	5.5682760000	-4.0951640000	-1.2161890000
Si	4.2601040000	-3.3778830000	-1.2307070000
Si	4.6163610000	-2.0865310000	2.5009370000
Si	5.8979690000	0.0562720000	-0.4686670000
H	7.2200300000	-0.6289420000	-0.3583370000
Si	-3.3282850000	-2.6479040000	1.3483150000
H	-2.5341870000	-1.0084760000	4.0171780000
Si	-1.7381170000	0.8014530000	1.4946500000
Si	0.1556240000	-2.2003290000	2.8801790000
Si	1.4059110000	-0.9011620000	4.3693120000
Si	-1.9824470000	-1.2481920000	2.6522340000
Si	-0.7571460000	2.2565950000	3.1027910000
Si	6.2313030000	2.2415030000	-1.2570900000
H	7.1130360000	2.9926740000	-0.3214290000
H	-1.4179490000	2.2639060000	4.4428670000
Si	-0.2389460000	4.4703200000	2.5077680000
H	0.4885430000	5.0931290000	3.6479460000
H	3.3672310000	-3.2095760000	5.2236790000
H	5.9428500000	-2.7373500000	2.7075270000
H	0.7334980000	-0.8838680000	5.7006860000
Si	3.5364400000	-1.8764120000	4.5817410000
H	4.4046160000	-1.0578890000	5.4732760000
Si	-2.3077070000	-2.4243680000	-0.7443330000
H	-3.0971850000	-3.0388750000	-1.8507700000
N	-2.9340330000	0.8160220000	0.1134660000
C	-4.3340070000	0.8773210000	0.2291690000
C	-4.9470680000	1.3157690000	1.4074870000
C	-5.1689370000	0.4996220000	-0.8284580000
C	-6.3270960000	1.3271730000	1.5372240000
H	-4.3346910000	1.6472080000	2.2431310000
C	-6.5498120000	0.5355510000	-0.7112380000
H	-4.7304800000	0.1929720000	-1.7758000000
C	-7.1553580000	0.9336280000	0.4839840000
H	-6.7730810000	1.6475530000	2.4749010000
H	-7.1655690000	0.2686450000	-1.5624620000
N	-8.5457180000	1.0174590000	0.6314190000
H	-8.8754170000	1.7116200000	1.2842530000

C	-9.5224740000	0.1661380000	0.1168090000
C	-9.2355430000	-1.1098460000	-0.3807530000
C	-10.8558440000	0.5957150000	0.1324560000
C	-10.2589530000	-1.9170150000	-0.8612210000
H	-8.2164860000	-1.4774670000	-0.3712750000
C	-11.8693930000	-0.2253000000	-0.3365160000
H	-11.0891760000	1.5872600000	0.5121460000
C	-11.5804320000	-1.4874450000	-0.8456280000
H	-10.0141350000	-2.9044570000	-1.2415530000
H	-12.8950640000	0.1307090000	-0.3109510000
H	-12.3731700000	-2.1259350000	-1.2208570000