Supplementary Information to "C atoms versus Si atoms at the bridgehead positions of phenyl-decorated adamantane-type clusters: Influence on the nonlinear optical response"

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simone.sanna@theo.physik.uni-giessen.de

Atom coordinates

Second entry for each structure is from a HSE06 calculation.

$[(PhSi)_4S_6]$

```
ATOMIC_POSITIONS angstrom
Si 19.8345964543 18.1444819582 20.1126896190
Si 17.0953743560 19.8513052094 19.1555700302
Si 17.6948562038 16.7933967453 17.9203170289
Si 19.6260961434 19.3887263948 17.0042905119
H 21.8196072306 19.8417625467 21.4484188041
H 23.2416107886 19.5644253689 23.4584509180
H 23.1968794192 17.4260738703 24.7351209032
H 21.7270621782 15.5617487584 23.9854460753
H 20.3006565805 15.8309692384 21.9783486837
H 16.3132644642 22.7042974553 18.5692822641
H 14.5733145270 24.1875291936 19.5234275721
H 13.0333390189 23.3377828126 21.2851349365
H 13.2392846557 20.9892511535 22.0897460325
H 14.9767771246 19.4990429886 21.1416094093
H 18.8722106997 14.1648112401 17.3271746057
H 17.9756377233 12.0612862102 16.3738247705
H 15.5627912170 11.8862402574 15.7810208546
H 14.0478759283 13.8268350530 16.1535228206
H 14.9360996961 15.9350624210 17.1030933696
H 19.4299559084 19.1747967881 14.0427165540
H 20.6391113389 20.2681227022 12.1795675431
H 22.4617725067 21.8972577303 12.6564426885
H 23.0701834811 22.4259376969 15.0126389481
H 21.8677493879 21.3339334763 16.8835740347
C 20.9632550674 17.8530610300 21.5679852784
C 21.7988764269 18.8992136155 21.9996435143
C 22.5992732375 18.7454853036 23.1320680374
C 22.5738017844 17.5451421029 23.8477856204
C 21.7489985938 16.4988704879 23.4278124908
C 20.9472358498 16.6516999809 22.2945952492
C 15.7644018999 20.9954862223 19.7838097247
C 15.6399466559 22.3208795081 19.3382469956
C 14.6606126380 23.1591093632 19.8761195235
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 C 13.7968740935 22.6819217991 20.8648358914
 C 13.9114436107 21.3641067766 21.3168225752
 C 14.8892976109 20.5260643173 20.7805683738
 C 16.9661168681 15.1981188341 17.2864496538
 C 17.8124630819 14.0950003489 17.0730610818
 C 17.3094751111 12.9097053429 16.5353360521
 C 15.9552945766 12.8122602078 16.2032625339
 C 15.1050317181 13.9008735641 16.4117154032
 C 15.6072488885 15.0879749419 16.9492350493
 C 20.5638647938 20.1750617160 15.5961093663
 C 20.2278473213 19.8867944704 14.2622828728
 C 20.9078474780 20.5029773061 13.2102959108
 C 21.9300505684 21.4166027957 13.4787193999
 C 22.2718412764 21.7135818554 14.8008901127
 C 21.5930264623 21.0974634733 15.8535995179
 S 18.3504216028 19.5003743256 20.8566999756
 S 19.0047742288 16.2526638124 19.5362721936
 S 21.0455513759 19.0271694964 18.5724479964
 S 16.0797939117 18.0594357085 18.5291744991
 S 18.1212989027 20.8268319762 17.5513867003
 S 18.7808919612 17.5764046881 16.2408047087


Si   H    C    S
4    20    24     6
Direct
  0.5340626293448646  0.4888620775811461  0.5415112961329610
  0.4605502422211593  0.5344510323901385  0.5159267094057174
  0.4767742761516582  0.4525883331728912  0.4827397244483840
  0.5283762290599118  0.5222308332985566  0.4582327888582096
  0.5874235574831663  0.5341212035672410  0.5773146017206365
  0.6255810388017621  0.5265001550993081  0.6309462209015012
  0.6243808310064597  0.4691994182519585  0.6649745905055058
  0.5849230578366252  0.4194260215307513  0.6448955154636593
  0.5466307284134260  0.4268032795621326  0.5913608486021932
  0.4395328830873189  0.6107367015037207  0.5000107318280086
  0.3930171170919100  0.6505090414763625  0.5253609500740531
  0.3517462043866093  0.6279596832053989  0.5725338844420774
  0.3571038311654592  0.5651462340795320  0.5941848698745102
  0.4035461137093868  0.5251552850083222  0.5690065416960616
  0.5082031760384289  0.3820656222523838  0.4668948698056529
  0.4840880136162010  0.3257753406348013  0.4416076487853065
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0.4194815784447688	0.3211361432498471	0.4258957746509904
0.3790404469562116	0.3731499188653827	0.4357719814699166
0.4029027960000788	0.4295616256286406	0.4609750542326151
0.5232425930225003	0.5166805806753960	0.3788540440391687
0.5557545037830413	0.5459162292793721	0.3291342804986578
0.6046085279098726	0.5893650598799141	0.3420505892348489
0.6207874086717675	0.6034124269570372	0.4051431780855660
0.5884788159737498	0.5742253182620386	0.4550836460370307
0.5643628178063760	0.4809407565033399	0.5804033527977459
0.5868230560352109	0.5088515279684745	0.5919818186461279
0.6083260835056062	0.5046456564932319	0.6222109742786306
0.6076407119416147	0.4724764409753963	0.6412878157816595
0.5854999436666393	0.4445416849425600	0.6300403425243742
0.5639612210781866	0.4487519886578741	0.5997847083899109
0.4248217967925534	0.5650691144533998	0.5326067415300731
0.4215078457706344	0.6005066751739919	0.5205903217280524
0.3953052177595225	0.6230149518681141	0.5348768699466377
0.3721516109103823	0.6103437434753397	0.5613383502748188
0.3751408675711862	0.5750952140246454	0.5735114435047554
0.4013082445424390	0.5526144266253905	0.5592531112546352
0.4572380506978593	0.4098417906995410	0.4658662570610484
0.4798186976038902	0.3802594300843412	0.4601823664531524
0.4663073639367341	0.3485136621910421	0.4459103892534580
0.4300439009514171	0.3459327997092411	0.4371033742308590
0.4073396253296582	0.3751039892560639	0.4426324904912825
0.4208609412952993	0.4068891098179490	0.4569090325691809
0.5535378051815165	0.5433041467654793	0.4205711452065224
0.5446110984457585	0.5356711567570656	0.3848421081083881
0.5628944419717147	0.5521487470477261	0.3567354010083372
0.5902925046134497	0.5765195014326572	0.3640071456307226
0.5993887908149047	0.5844111391909080	0.3994139272889010
0.5811259148654725	0.5679210071402596	0.4275165562368082
0.4942764818390111	0.5250533237640901	0.5612561115170355
0.5118342238301482	0.4383772443449424	0.5259419501609411
0.5662123938919316	0.5124909766175965	0.5002115062126586
0.4336781681948427	0.4864582970764677	0.4991133384691568
0.4880396629919417	0.5604457955072296	0.4730404415481918
0.5057636710731420	0.4737537770249350	0.4379435385469845

$[(PhSi)_3(PhC)S_6]$

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ATOMIC_POSITIONS angstrom
Si 18.1432410016 20.1410357286 19.7088205473
Si 19.3200787940 17.1329194606 19.7875582587
Si 16.8536334702 17.8319244073 17.8129228632
H 19.2586347378 20.7495428436 15.2418242393
H 20.6951068140 21.5399395100 13.3861886956
H 23.0167683471 20.6557368312 13.1354362073
H 23.8712392461 18.9728874164 14.7648310296
H 22.4399903363 18.1853512592 16.6109240560
H 15.9409621615 22.1668342392 19.9693514370
H 15.7951732190 24.3412832622 21.1506263428
H 17.7482181304 25.2010453672 22.4325038979
H 19.8529718764 23.8736608628 22.5326700222
H 20.0017057839 21.6896541131 21.3677230238
H 20.3860690146 14.5404866984 18.9193125805
H 21.6442439655 12.7325355363 20.0586552089
H 22.2270296573 12.9456317667 22.4705807901
H 21.5600438380 14.9830346909 23.7360479780
H 20.3238392685 16.8050863156 22.5992731593
H 15.0822523003 15.4201092507 17.9438203958
H 13.0604530311 14.7479797699 16.6807878190
H 12.1860250723 16.1986221049 14.8559322295
H 13.3422216093 18.3335424740 14.3021860337
H 15.3528449533 19.0260564102 15.5771714650
C 19.8104187278 18.9766145769 17.1916841006
C 20.7448379963 19.4078921539 16.0533356718
C 20.2702253781 20.3584945294 15.1322333837
C 21.0810505074 20.8022909667 14.0904864254
C 22.3810943761 20.3072148414 13.9501154332
C 22.8586824848 19.3660384065 14.8609725654
C 22.0467899415 18.9178436142 15.9072928803
C 17.9801726095 21.7745931228 20.5888954595
C 16.8006562500 22.5349164072 20.5325223604
C 16.7176630579 23.7610828217 21.1955420904
C 17.8141285474 24.2430210379 21.9150248833
C 18.9954563311 23.4981586714 21.9729696140
C 19.0784664582 22.2702320406 21.3157353568
C 20.2674916866 15.8002345906 20.6800768021
C 20.6461989895 14.6427851384 19.9748023278
C 21.3519200492 13.6237353758 20.6153958291
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C 21.6799829028 13.7449120536 21.9687428012

C 21.3064870067 14.8883011700 22.6794651690

C 20.6076034482 15.9129314493 22.0377864724

C 15.3604264189 17.2703471875 16.8497277732

C 14.7044523246 16.0648065170 17.1479098228

C 13.5655225618 15.6831880489 16.4359063198

C 13.0749584259 16.4981640678 15.4126969572

C 13.7223396367 17.6975208675 15.1026088664

C 14.8554119314 18.0847252972 15.8191844538

S 19.5335126048 20.5548265332 18.1340782487

S 20.6498097583 17.6825657784 18.2022497302

S 18.3021815834 18.3290888422 16.3156161653

S 18.9219665662 18.7396707841 21.1435428492

S 16.2284836237 19.5392961393 18.9653090515

S 17.5072360187 16.2268852819 19.0721518316

Si H C S

3 20 25 6

Direct

0.4888794920760796 0.5423062986959859 0.5306632403748824

0.5203291389402429 0.4616089792059672 0.5326696814750991

0.4542074585033655 0.4805270431987397 0.4798667986919539

0.5186790786501845 0.5586387739180260 0.4110968641553573

0.5570726347283473 0.5796549040379616 0.3614306487186664

0.6191280023470740 0.5558210064081365 0.3546096797544687

0.6419349614798444 0.5107556920027249 0.3981922166141551

0.6037349859180356 0.4897914221028841 0.4476081684536997

0.4299124157607115 0.5964971359259676 0.5375477785565597

0.4258658115436183 0.6546711053904225 0.5690607227918083

0.4779874522600921 0.6777531811866953 0.6035169203811024

0.5343213273444966 0.6422777758501995 0.6064516516536550

0.5384843744752292 0.5838582328460996 0.5753501962600540

0.5485798499527668 0.3919072692722045 0.5096425323252807

0.5822243126422667 0.3436311633980596 0.5402272420391010

0.5981372875838270 0.3496342331498142 0.6046598185514895

0.5805429636103420 0.4043434475255538 0.6383362007032307

0.5474454925499674 0.4529869796711986 0.6078585355740986

0.4069916810251861 0.4157691216196281 0.4830883955047620

0.3530308124167224 0.3976806870812686 0.4492186219458570

0.3294181736713520 0.4366115093540453 0.4005896151193110

0.3600079162078236 0.4940060468900457 0.3860887474027235

0.4137036763426195 0.5126397884812324 0.4202315103266493

0.5332501026858649 0.5110901942529800 0.4633581014737067

0.5583710163075234 0.5226031974216213 0.4327968069977738

0.5457075337537721 0.5480698877480971 0.4081691896510256

0.5673786946617780 0.5598919702496175 0.3802609533265410

0.6021335317312152 0.5465507506500056 0.3764437185512320

0.6148739408211752 0.5213506527067295 0.4008004404877250

0.5931565714013459 0.5094117327707266 0.4288486927705690

0.4844526667229695 0.5860094633182259 0.5542736920035518

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0.4505572502665057 0.6391695582231652 0.5703667550689798

0.4798215255262890 0.6521023961596724 0.5897072744159755

0.5114434514742490 0.6321964828899965 0.5913958813480765

0.5137434450615088 0.5993292617762696 0.5738326489038347

0.5456522055635623 0.4259164919909855 0.5565926648959294

0.5556402153773118 0.3948127997205259 0.5378487137687417

0.5745250023822454 0.3675755573536769 0.5550307039512148

0.5834759657127307 0.3709809746303517 0.5911947894012270

0.5736319556655632 0.4016844065272734 0.6101071385856293

0.5549122587807663 0.4290538475803998 0.5928722424028521

0.4142361305330363 0.4654854887199811 0.4540771918949616

0.3968292783500056 0.4331056374166053 0.4618917693131501

0.3664019388985466 0.4228137061169298 0.4427968726904738

0.3531560219484525 0.4446878139183901 0.4155335451964540

0.3702907918767920 0.4769295525283863 0.4074037932313627

0.4005668224439169 0.4873354708533332 0.4266214207756533

0.5259782023154376 0.5531409956541692 0.4884427068717576

0.5556771861160374 0.4765541460280380 0.4902077334469728

0.4930885057778206 0.4938917160852456 0.4400142500513177

0.5096997616182575 0.5046585729228793 0.5687765216116398

0.4377471841679545 0.5261325654827852 0.5107802121510571

0.4717988705949429 0.4376730037753651 0.5134828172038313

$[(\mathbf{PhSi})_2(\mathbf{PhC})_2\mathbf{S}_6]$

ATOMIC_POSITIONS angstrom

Si 19.9912218449 19.8909928702 18.9029704218

Si 18.5548156820 18.2868240803 16.6134129665

H 14.6442060504 17.8624106413 18.6330096536

H 12.3817138110 18.2322060811 19.5744578415

H 11.9848938249 20.0987706188 21.1830200115

H 13.8853433506 21.5675703996 21.8533654292

H 16.1423580108 21.1843774846 20.9312127147

H 18.9624035904 14.2858972708 18.7583575265

H 19.1403547734 12.3469188480 20.2752481072

H 19.3470780976 12.6875974808 22.7361874094

H 19.3796509850 15.0070203715 23.6587713265

H 19.2261720491 16.9534552144 22.1320471028

H 20.1322324350 22.7913489193 18.4678044254

H 21.7701723125 24.5407712238 19.1009232131

H 23.8062419875 23.9341219485 20.4002122339

H 24.1896438182 21.5701909707 21.0798897586

H 22.5482876679 19.8188378347 20.4740216727

H 20.3106476954 18.5263181448 14.2289994151

H 20.0601468547 17.8297941259 11.8637329451

H 17.9721051663 16.7040301416 11.1078047032

H 16.1369080840 16.2648226450 12.7318526506

H 16.3867448816 16.9448995871 15.1056213687

C 16.9338048887 19.2131458904 19.1171219760

C 18.9672002561 16.9959669072 19.4470673384

C 15.5467124268 19.5086928067 19.7018174673

C 14.4735696430 18.6757555111 19.3379914103

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C 15.3202007160 20.5414524877 20.6196463495

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C 19.0617755754 14.4517045274 19.8302892843

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C 19.2932370006 14.8444395882 22.5840106628

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C 21.2213116115 21.1820845065 19.4317942269

C 21.0170085801 22.5199917618 19.0478777359

C 21.9400916487 23.5057258938 19.3999675498

C 23.0818705091 23.1646069488 20.1302170731

C 23.2973406162 21.8381654897 20.5128219549

C 22.3706523644 20.8521300151 20.1689208734

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C 19.3937368735 18.0294046117 13.9057603658

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C 18.0825328826 17.0053377683 12.1503374036
C 17.0519714208 16.7581770185 13.0617189465
C 17.1923692995 17.1425770955 14.3959660950
S 17.3339261294 17.6448266720 19.9901578049
S 18.0759369816 20.6081934947 19.5290024891
S 16.6804700170 19.0671357869 17.2766391938
S 20.4393860888 18.0540604448 19.8922565699
S 19.0148928452 16.4873359350 17.6734863834
S 20.1275892785 19.7327208472 16.7647642893
```

```
Si   H    C    S
2    20    26     6
Direct
  0.5382728483018707  0.5355573551650422  0.5091217938655941
  0.4997912648046049  0.4925445993659905  0.4477164389368771
  0.3952847386986583  0.4811867116629001  0.5018535880493359
  0.3347743945270901  0.4909778752638845  0.5269927450557055
  0.3240610268869840  0.5408793349818587  0.5700891216912586
  0.3748294327519013  0.5802836757839578  0.5879981221867825
  0.4351754266009067  0.5702413441831050  0.5633306641478542
  0.5103720780831938  0.3854639002833836  0.5052201580695197
  0.5151365605340713  0.3336837913354034  0.5458116756318596
  0.5209534747102923  0.3428202319751962  0.6116332073759850
  0.5219838481273348  0.4049040984162409  0.6362731406864049
  0.5177663964655667  0.4569310109471693  0.5954632125500804
  0.5423083690653397  0.6131251117904719  0.4972130585404244
  0.5860383722758431  0.6599318419680648  0.5142614267394635
  0.6402407924968202  0.6438001790502217  0.5495075527969283
  0.6502988139768751  0.5806234839644497  0.5680676442576525
  0.6065107800873358  0.5337404557297384  0.5517191240628011
  0.5464623211667966  0.4992235245959326  0.3835748249285519
  0.5395967386372394  0.4804672915806918  0.3203815814985747
  0.4838269602496881  0.4499619963984031  0.3004400463272316
  0.4349651357121013  0.4380008220415173  0.3441107080307467
  0.4417694229514908  0.4563463276700611  0.4075256961353603
  0.4566204714263972  0.5173569048962239  0.5147126794044741
  0.5107659363239532  0.4582220040045591  0.5235320471110345
  0.4193893986013003  0.5253036832912895  0.5304173370534502
  0.3907206671734408  0.5029706715465029  0.5206919907554209
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0.4132870827510248 0.5529275735605813 0.5549603404273579

0.5140493022905225 0.4248828036127644 0.5474619600514871

0.5131281691821868 0.3900102368949510 0.5338677581640004

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$[(\mathbf{PhSi})(\mathbf{PhC})_3\mathbf{S}_6]$

ATOMIC_POSITIONS angstrom

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$[(\mathbf{PhC})_4\mathbf{S}_6]$

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HOMO / LUMO Plots

The isosurface for the HOMO / LUMO plots is 0.001 eV/Å^3

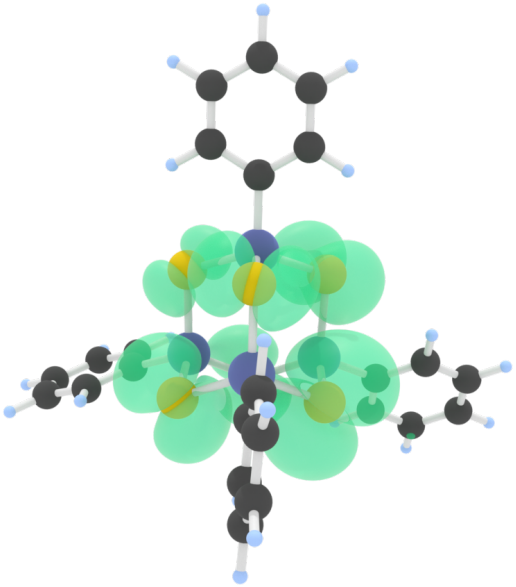

Figure 1: HOMO of $[(PhSi)_4S_6]$

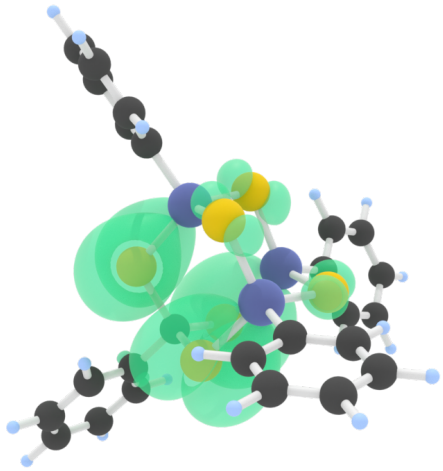

Figure 2: HOMO of $[(PhSi)_3(PhC)S_6]$

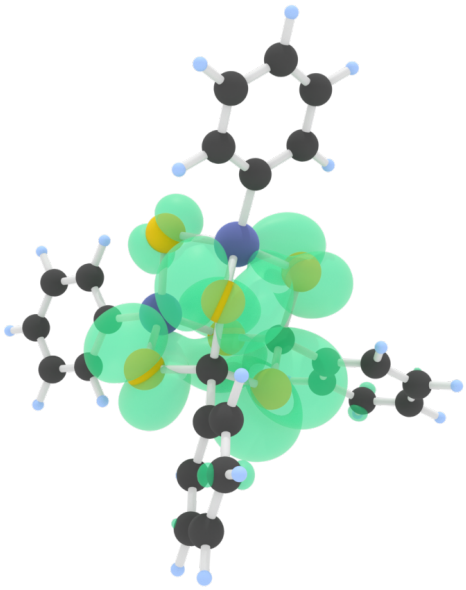

Figure 3: HOMO of $[(PhSi)_2(PhC)_2S_6]$

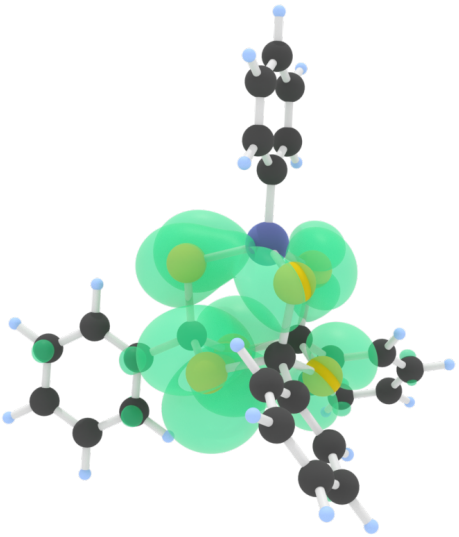

Figure 4: HOMO of [(PhSi)$(PhC)_3S_6$]

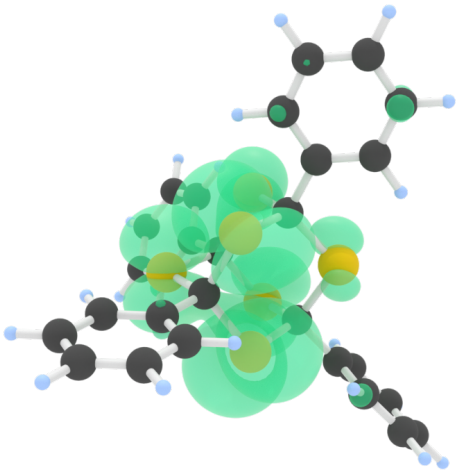

Figure 5: HOMO of [$(PhC)_4S_6$]

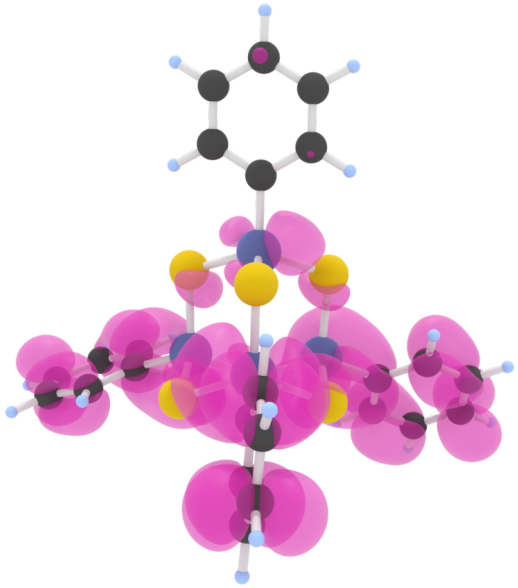

Figure 6: LUMO of $[(PhSi)_4S_6]$

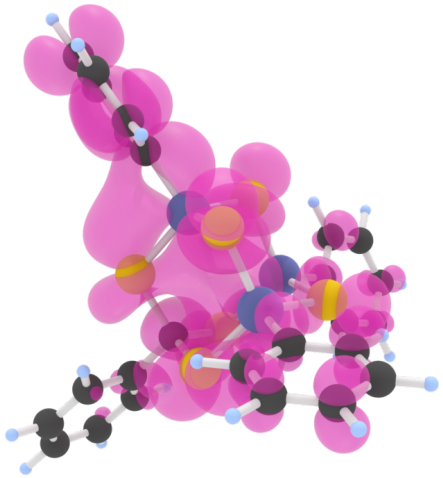

Figure 7: LUMO of $[(PhSi)_3(PhC)S_6]$

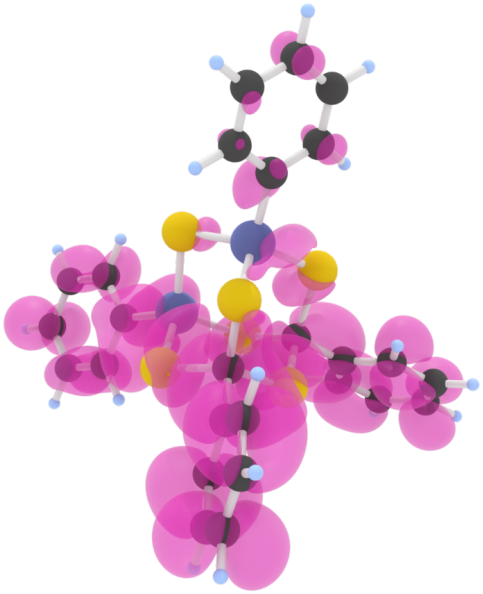

Figure 8: LUMO of $[(PhSi)_2(PhC)_2S_6]$

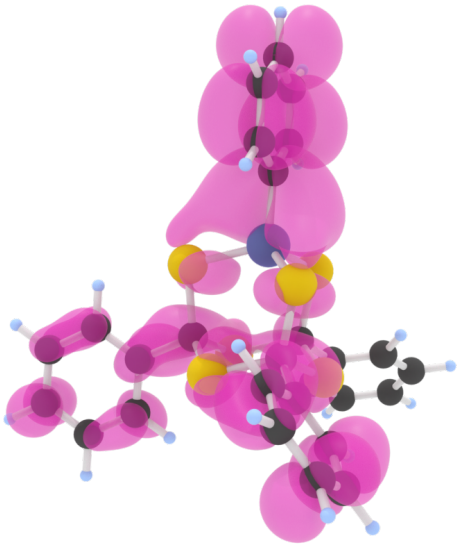

Figure 9: LUMO of $[(PhSi)(PhC)_3S_6]$

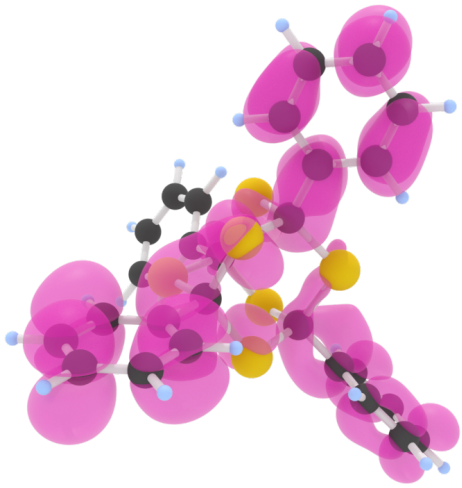

Figure 10: LUMO of $[(PhC)_4S_6]$

Computational approach and main computational parameters for non-linear optical calculations.

Within the present approach, the nonlinear optical susceptibility $\chi^{(n)}$ is obtained in the time domain from the dynamical polarization $\vec{P}$ of the system, using the expansion of $\vec{P}$ in power of the applied field $\vec{E}$. The Cartesian component α reads

$$P_\alpha = \sum_\beta \chi^{(1)}_{\alpha\beta} E_\beta + \sum_{\beta,\gamma} \chi^{(2)}_{\alpha\beta\gamma} E_\beta E_\gamma + \sum_{\beta,\gamma,\delta} \chi^{(3)}_{\alpha\beta\gamma\delta} E_\beta E_\gamma E_\delta + \dots . \tag{1}$$

The starting point of the calculation is the the zero-field Kohn-Sham Hamiltonian

$$\hat{H}^0 = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \hat{V}_{\text{el}} + \hat{V}_{\text{H}}[\rho_0] + \hat{V}_{\text{xc}}[\rho_0], \tag{2}$$

where $\hat{V}_{\text{el}}$ is the electron-ion interaction, $\hat{V}_{\text{H}}$, and $\hat{V}_{\text{xc}}$ are the Hartree and the exchange-correlation potentials, respectively.

The (external, monochromatic) laser excitation

$$\vec{E}(t) = \vec{E}_0 \sin(\omega_L t) \tag{3}$$

with the frequency ω_L is used for the definition of the non-hermitian field coupling operator

$$\hat{w}_{\vec{k}} = \frac{ief}{4\pi} \sum_m \sum_{\alpha=1}^{3} (\vec{a}_\alpha \cdot \vec{E}) N_{\vec{k}_\alpha} \sum_{\sigma=\pm} \sigma |\tilde{v}_{\vec{k}^\sigma_\alpha,m}\rangle\langle v_{\vec{k},m}|. \tag{4}$$

In this equation

$$|\tilde{v}_{\vec{k}^\pm_\alpha,n}\rangle = \sum_m (S(\vec{k}, \vec{k}^\pm_\alpha)^{-1})_{mn} |v_{\vec{k}^\pm_\alpha,m}\rangle. \tag{5}$$

The matrix S is built up by the overlaps of the periodic part of the occupied Bloch functions $v_{\vec{k},m}$:

$$S_{mn}(\vec{k}, \vec{k} + \vec{q}_\alpha) = \langle v_{\vec{k},m} | v_{\vec{k}+\vec{q}_\alpha,n}\rangle. \tag{6}$$

The latter are obtaining by solving the equation of motions

$$i\hbar \frac{d}{dt} |v_{\vec{k},m}\rangle = (\hat{H}^0_{\vec{k}} + \hat{w}^\dagger_{\vec{k}}(\vec{E}))|v_{\vec{k},m}\rangle \tag{7}$$

in the time domain. Finally, the polarization

$$\vec{P}_\alpha = -\frac{ef}{2\pi v} \frac{\vec{a}_\alpha}{N_{\vec{k}^\perp_\alpha}} \sum_{\vec{k}^\perp_\alpha} \mathrm{Im} \left[\sum_{i=1}^{N_{\vec{k}^\perp_\alpha}-1} \mathrm{Tr} \ln S(\vec{k}_i, \vec{k}_i + \vec{q}_\alpha) \right] \tag{8}$$

is calculated, from which the non-linear susceptibility can be obtained. The procedure is repeated for all required excitation frequencies.

In this computational procedure, general parameters were converged for the SHG response. Effective parameters chosen were identified through multiple convergence tests

weighting the numerical cost to accuracy of the results. Orbitals are set by an interval including a factor for the lowest and highest orbital. The interval of $(0.2, 0.8)$ orbitals when the interval of $(0, 1)$ orbitals range from 1 to $3 \times$ number of occupied orbitals for frequencies with energies ≥ 5 eV, linear interpolated between $2 \times$ number of occupied orbitals, and $3 \times$ number of occupied orbitals for energies within (2 eV,3 eV), and $2 \times$number of occupied orbitals for energies ≥ 0 eV. G-Vectors were reduced down to a minimum of ≈ 0.014 times, and in their maximum 0.5 times an energy cutoff of 80 Ry. Occasionally these parameters were/could be tweaked as they tend to overestimate the necessary accuracy needed for intended evaluation. The volumes within the molecules are simulated are 51179,6 $Å^3$ dependent on molecule size. Field intensity was chosen to be 0.100000E+8 kW/cm^2.

Further numerical parameters

The spectral broadening within YAMBO is set to 0.2 eV.

Further computational parameters vary for each structure, due to the stepwise process. Therefore, we give a range (min,max) for each structure.

$[(PhSi)_4S_6]$

Simulation times: 43.2999990474 fs , 43.2999990474 fs

Step time: 0.00999999978 fs , 0.00999999978 fs

Kinetic-energy cutoff (QE): 1088.4554498392001 eV

$[(PhSi)_3(PhC)S_6]$

Simulation times: 43.2999990474 fs , 43.2999990474 fs

Step time: 0.00999999978 fs , 0.00999999978 fs

Kinetic-energy cutoff (QE): 1088.4554498392001 eV

$[(PhSi)_2(PhC)_2S_6]$

Simulation times: 43.2999990474 fs , 43.2999990474 fs

Step time: 0.00999999978 fs , 0.00999999978 fs

Kinetic-energy cutoff (QE): 1088.4554498392001 eV

$[(PhSi)_1(PhC)_3S_6]$

Simulation times: 43.2999990474 fs , 43.2999990474 fs

Step time: 0.00999999978 fs , 0.00999999978 fs

Kinetic-energy cutoff (QE): 1088.4554498392001 eV

$[(PhC)_4S_6]$

Simulation times: 43.2999990474 fs , 43.2999990474 fs

Step time: 0.00999999978 fs , 0.00999999978 fs

Kinetic-energy cutoff (QE): 1088.4554498392001 eV

k-Point Grid

The Gamma point sampling was employed for the structural optimization of the isolated clusters. A regular 2x2x2 k-point mesh is furthermore needed for the converged calculation of the dynamical polarization and was thus employed for the calculation of the optical response of all investigated structures.

Coloring of the orbital (overlaps)

The overlap $(\rho_1 \cdot \rho_2)$ in the range from the numerical values 0.0 $\left(\frac{\text{eV}}{\text{Å}^3}\right)^2$ to 0.05 $\left(\frac{\text{eV}}{\text{Å}^3}\right)^2$ is colored from "low" to "high" by the RGB values from (1.0, 1.0, 1.0) to (0.0, 0.0, 0.0). This color code is The presented isosurfaces is the $\frac{1}{32}$ of the maximum value of the distribution.

Visual representation of the core distortion

The bridgehead atoms $Si_{4-x}C_x$ $x = 0, \ldots, 4$ (i.e., the core skeleton of the investigated compounds) define a more or less distorted tetrahedron (or rather a trigonal pyramid), as shown in the following picture on the example of the $[(PhSi)_4S_6]$ molecular cluster.

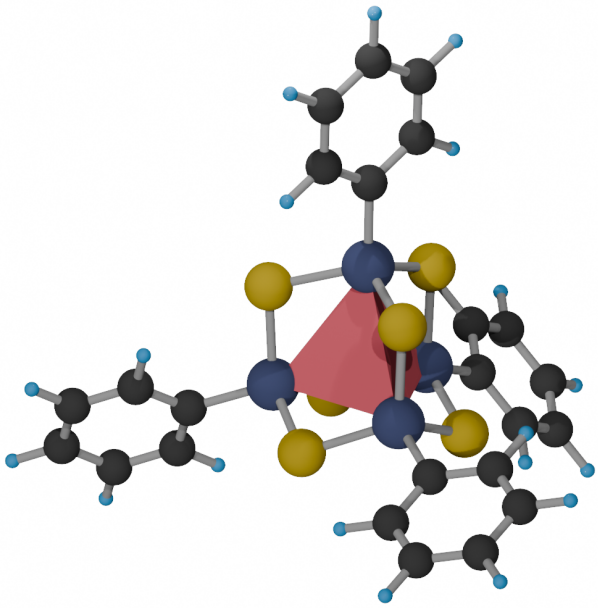

Figure 11: $[(PhSi)_4S_6]$ molecular cluster, with the tetrahedron described by the bridgehead atoms highlighted in the cluster core.

Structural distortions can be visualized, e.g., by the deviation of the calculated bridgehead atom positions from an ideal tetrahedron. Keeping the color coding employed in Fig. 2 or 3 of the manuscript ($[(PhC)_4S_6]$ in **violet**, $[(PhSi)(PhC)_3S_6]$ in **red**, $[(PhSi)_2(PhC)_2S_6]$ in **green**, $[(PhSi)_3(PhC)S_6]$ in **orange**, and $[(PhSi)_4S_6]$ in **blue**) the visual comparison of the tetrahedron distortion is obtained:

Figure 12: Comparison of the tetrahedra described by the bridgehead atoms highlighted in the cluster core.

The shaded region represents an ideal, regular tetrahedron with the volume of the pyramid inscribed in $[(PhC)_4S_6]$ (in violet), showing that nearly no distortion occurs for this compound. The same holds for $[(PhSi)_4S_6]$ (in blue). All other structures show a more or less pronounced distortion, instead.

Hybrid-DFT

Further calculations using HSE06 hybrid functional were conducted to address the question whether a more precise description of the electronic structure would change the interpretations/conclusions made in the manuscript.

The effect of the hybrid calculations on the electronic structure is both to open the HOMO-LUMO gap (see table below) and to slightly broaden the energy window in which

orbital groups are distributed. This is illustrated on the example of the (occupied) energy levels we associate with the first SHG peak.

Table 1: HOMO-LUMO gaps as calculated within DFT-PBE and HSE06 for the investigated compounds. All values are given in eV.

Compound	PBE [eV]	HSE06 [eV]
$[(SiPh)_4S_6]$	3.80	5.06
$[(SiPh)_3(CPh)S_6$	3.28	4.56
$[(SiPh)_2(CPh)_2S_6]$	3.25	4.53
$[(SiPh)(CPh)_3S_6]$	3.20	4.46
$[(CPh)_4S_6]$	3.15	4.44

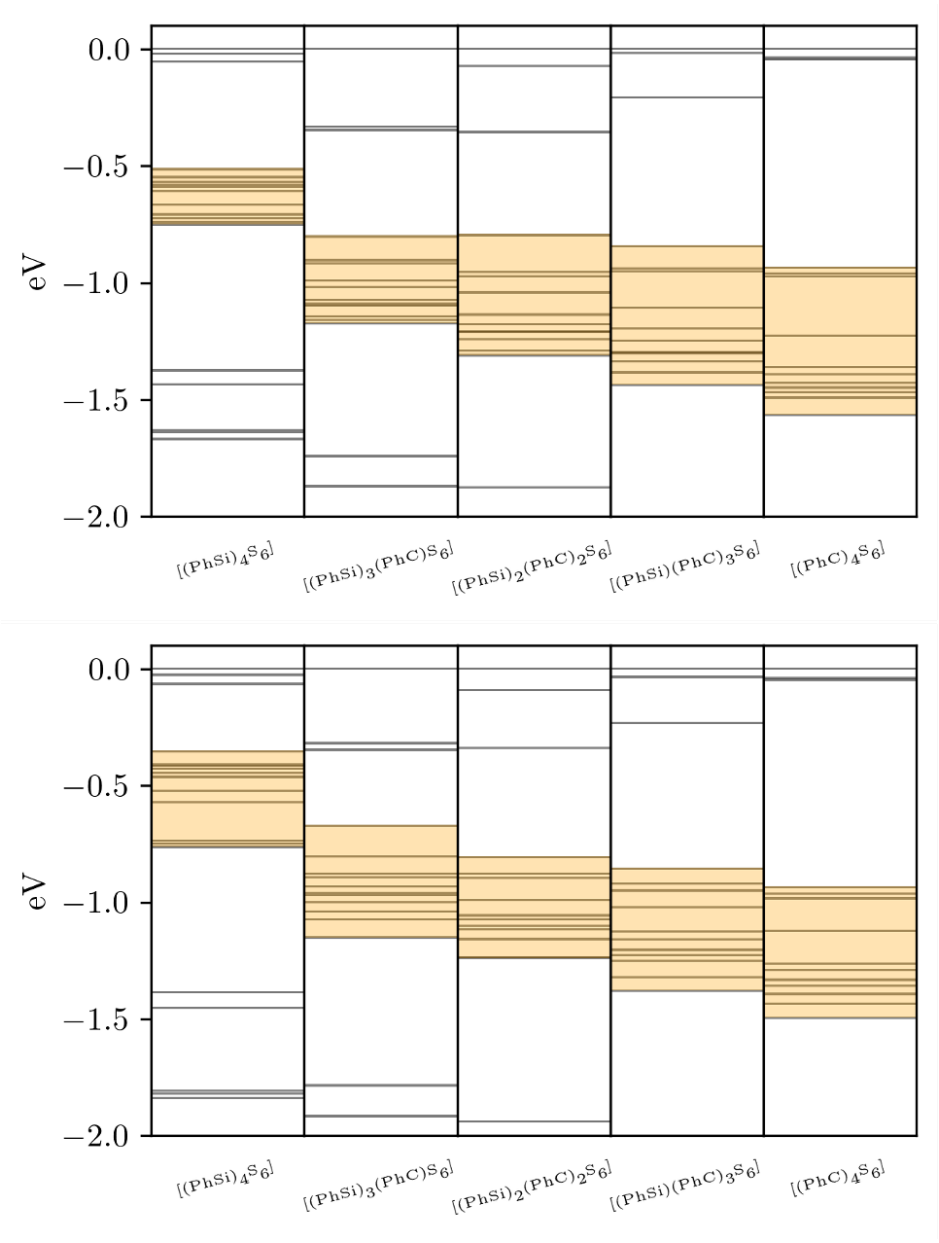

Figure 13: Occupied electronic levels of the investigated molecular clusters as calculated within DFT-PBE (upper panel) and hybrid-DFT in the HSE06 formulation. The orbital group associated to the SHG response in the region below 3 eV is highlighted. It contains 11 individual electronic levels and widens from left to right. The same 11 levels can be discriminated both in the PBE and HSE06 calculations. The origin of the energy scale is the HOMO level.

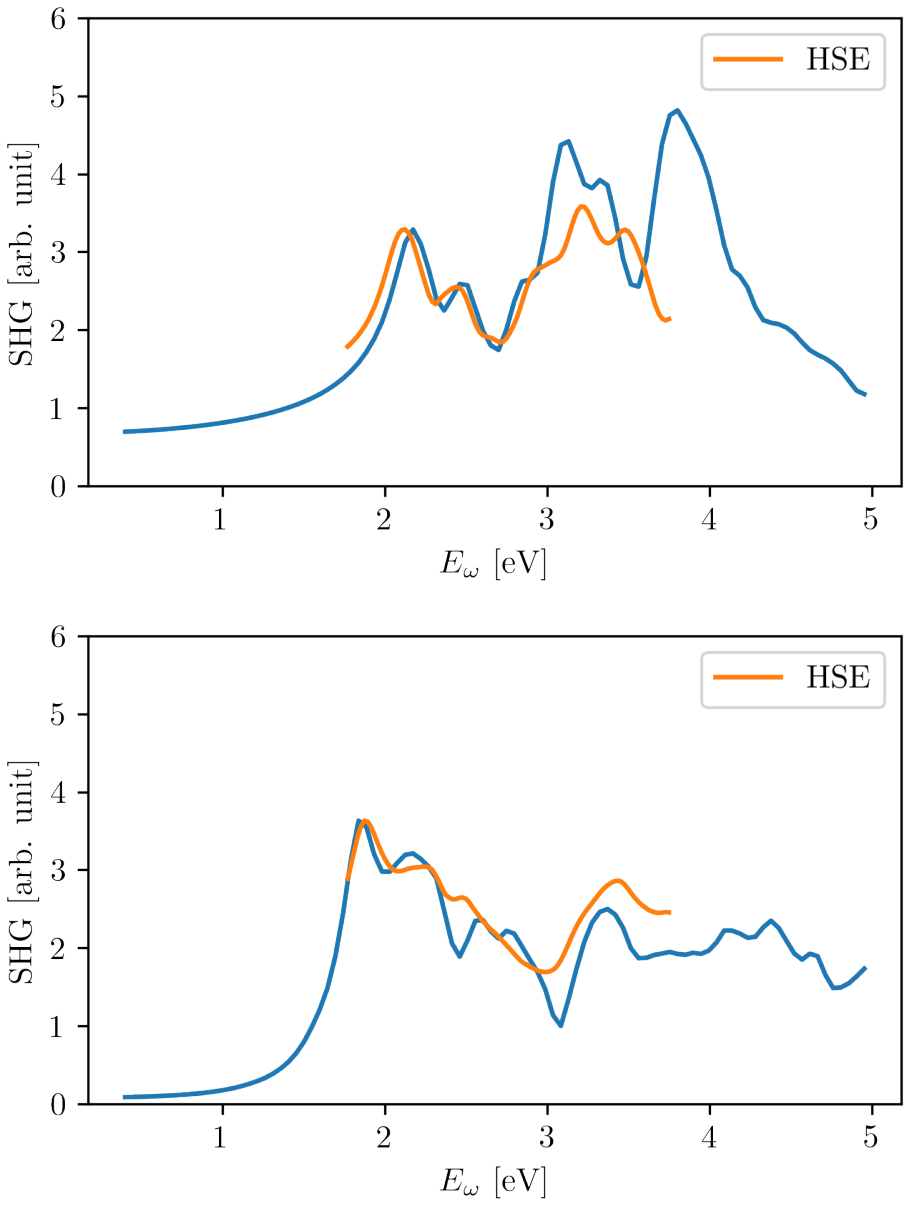

Figure 14: Comparison of the SHG spectra as calculated within DFT-PBE (blue line) and hybrid-DFT in the HSE06 formulation (orange line) for $[(SiPh)_4S_6]$ (upper panel) and $[(CPh)_4S_6]$ (lower panel). The HSE06 spectra are shifted by a value corresponding to the HOMO-LUMO gap difference between PBE and HSE06 for a better comparison.