Optical absorption of warped nanographenes tuned by five- and seven-membered carbon rings

Xinqin Wang, a Shengping Yu, b Zhaoyang Lou, a Qun Zeng, a and Mingli Yang* a

a Institute of Atomic and Molecular Physics, Key Laboratory of High Energy Density Physics and Technology of Ministry of Education, Sichuan University, Chengdu 610065, P. R. China

b College of Chemistry and Environment Protection Engineering, Southwest University for Nationalities, Chengdu 610041, P. R. China
**Table S1** The HOMO, LUMO energy levels and their gaps (in eV) calculated with B3LYP/def-TZVP.

**Table S2** Compositions of HOMO to LUMO transitions.

**Fig. S1** Optimized structure of C₈₀H₃₀. Values in red are the dihedral angles (in degree) of the structure obtained with B3LYP/def-TZVP.

**Fig. S2** Projected density of states (PDOS) of C₈₀H₃₀ and C₇₈H₈₀.

**Fig. S3** The UV/Vis absorption spectra of C₈₀H₃₀ calculated with various functionals of B3LYP, Cam-B3LYP, PBE, PBE0, M06-2X and TPSSh.

**Fig. S4** HOMO and LUMO orbitals of a–e.

**Fig. S5** HOMO and LUMO orbitals of a’–e’.

**Fig. S6** HOMO and LUMO contours of the model molecules shown in Fig. 4.
Table S1 The HOMO, LUMO energy levels and their gaps (in eV) calculated with B3LYP/def-TZVP.

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
<th>Gaps</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Gaps</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{80}H_{30}</td>
<td>-5.336</td>
<td>-2.329</td>
<td>3.007</td>
<td>C_{78}H_{30}</td>
<td>-5.168</td>
<td>-2.263</td>
</tr>
<tr>
<td>a</td>
<td>-5.276</td>
<td>-2.406</td>
<td>2.870</td>
<td>a'</td>
<td>-5.355</td>
<td>-2.396</td>
</tr>
<tr>
<td>b1</td>
<td>-5.256</td>
<td>-2.429</td>
<td>2.827</td>
<td>b1'</td>
<td>-5.221</td>
<td>-2.332</td>
</tr>
<tr>
<td>b2</td>
<td>-5.214</td>
<td>-2.402</td>
<td>2.812</td>
<td>b2'</td>
<td>-5.363</td>
<td>-2.393</td>
</tr>
<tr>
<td>c</td>
<td>-5.327</td>
<td>-2.496</td>
<td>2.830</td>
<td>c'</td>
<td>-5.416</td>
<td>-2.410</td>
</tr>
<tr>
<td>d</td>
<td>-5.250</td>
<td>-2.454</td>
<td>2.795</td>
<td>d'</td>
<td>-5.338</td>
<td>-2.365</td>
</tr>
<tr>
<td>e</td>
<td>-5.398</td>
<td>-2.513</td>
<td>2.884</td>
<td>e'</td>
<td>-5.500</td>
<td>-2.408</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td>β</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C₈₀H₃₀</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>485.56nm</td>
<td>f=0.1772</td>
<td>435.53nm</td>
<td>f=0.5851</td>
<td>335.72nm</td>
<td>f=0.2725</td>
<td></td>
</tr>
<tr>
<td>HOMO:255</td>
<td>254 → 257</td>
<td>0.192</td>
<td>252 → 256</td>
<td>-0.206</td>
<td>249 → 257</td>
<td>-0.114</td>
</tr>
<tr>
<td>LUMO:256</td>
<td>255 → 256</td>
<td>0.668</td>
<td>253 → 256</td>
<td>-0.195</td>
<td>252 → 258</td>
<td>-0.148</td>
</tr>
<tr>
<td></td>
<td>254 → 256</td>
<td>0.366</td>
<td>253 → 259</td>
<td>-0.396</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>255 → 257</td>
<td>0.507</td>
<td>255 → 260</td>
<td>-0.101</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>255 → 261</td>
<td>-0.105</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>255 → 263</td>
<td>0.431</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>255 → 265</td>
<td>-0.105</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C₇₈H₃₀</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>443.16nm</td>
<td>f=1.8478</td>
<td>443.16nm</td>
<td>f=1.8478</td>
<td>298.22nm</td>
<td>f=0.1942</td>
<td></td>
</tr>
<tr>
<td>HOMO:249</td>
<td>248 → 250</td>
<td>0.339</td>
<td>248 → 250</td>
<td>0.339</td>
<td>244 → 254</td>
<td>0.119</td>
</tr>
<tr>
<td>LUMO:250</td>
<td>248 → 251</td>
<td>0.363</td>
<td>248 → 251</td>
<td>0.363</td>
<td>247 → 253</td>
<td>0.354</td>
</tr>
<tr>
<td></td>
<td>249 → 250</td>
<td>0.360</td>
<td>249 → 250</td>
<td>0.360</td>
<td>248 → 261</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td>249 → 251</td>
<td>-0.339</td>
<td>249 → 251</td>
<td>-0.339</td>
<td>248 → 262</td>
<td>0.338</td>
</tr>
<tr>
<td></td>
<td>248 → 263</td>
<td>-0.155</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>249 → 261</td>
<td>0.349</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>249 → 262</td>
<td>-0.163</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a</strong></td>
<td>514.02nm</td>
<td>f=0.1315</td>
<td>458.77nm</td>
<td>f=0.6236</td>
<td>389.45nm</td>
<td>f=0.1076</td>
</tr>
<tr>
<td>HOMO:248</td>
<td>246 → 249</td>
<td>-0.108</td>
<td>246 → 249</td>
<td>0.171</td>
<td>241 → 249</td>
<td>-0.174</td>
</tr>
<tr>
<td>LUMO:249</td>
<td>247 → 250</td>
<td>0.242</td>
<td>247 → 249</td>
<td>0.433</td>
<td>242 → 249</td>
<td>-0.352</td>
</tr>
<tr>
<td></td>
<td>248 → 249</td>
<td>0.636</td>
<td>248 → 250</td>
<td>0.509</td>
<td>243 → 249</td>
<td>-0.229</td>
</tr>
<tr>
<td></td>
<td>244 → 250</td>
<td>0.424</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>247 → 251</td>
<td>0.121</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>247 → 253</td>
<td>-0.111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>248 → 252</td>
<td>0.130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>b₁</strong></td>
<td>522.13nm</td>
<td>f=0.0657</td>
<td>464.41nm</td>
<td>f=0.5894</td>
<td>351.26nm</td>
<td>f=0.1434</td>
</tr>
<tr>
<td>HOMO:241</td>
<td>240 → 242</td>
<td>0.225</td>
<td>238 → 242</td>
<td>-0.268</td>
<td>234 → 242</td>
<td>-0.100</td>
</tr>
<tr>
<td>LUMO:242</td>
<td>240 → 243</td>
<td>0.255</td>
<td>238 → 243</td>
<td>0.125</td>
<td>238 → 244</td>
<td>-0.112</td>
</tr>
<tr>
<td></td>
<td>241 → 242</td>
<td>0.569</td>
<td>239 → 242</td>
<td>-0.111</td>
<td>238 → 245</td>
<td>-0.125</td>
</tr>
<tr>
<td></td>
<td>241 → 243</td>
<td>-0.209</td>
<td>240 → 242</td>
<td>0.378</td>
<td>239 → 244</td>
<td>-0.276</td>
</tr>
<tr>
<td></td>
<td>241 → 243</td>
<td>0.475</td>
<td>239 → 247</td>
<td>0.100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>240 → 246</td>
<td>-0.139</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>240 → 248</td>
<td>0.260</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>241 → 246</td>
<td>-0.228</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>241 → 248</td>
<td>0.380</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>241 → 249</td>
<td>-0.124</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>b₂</strong></td>
<td>518.76nm</td>
<td>f=0.2384</td>
<td>456.17nm</td>
<td>f=0.5224</td>
<td>389.37nm</td>
<td>f=0.0970</td>
</tr>
<tr>
<td>HOMO:241</td>
<td>240 → 242</td>
<td>-0.182</td>
<td>240 → 242</td>
<td>-0.471</td>
<td>236 → 242</td>
<td>0.514</td>
</tr>
<tr>
<td>LUMO:242</td>
<td>241 → 242</td>
<td>0.669</td>
<td>241 → 243</td>
<td>0.491</td>
<td>237 → 243</td>
<td>0.103</td>
</tr>
<tr>
<td></td>
<td>241 → 244</td>
<td>0.137</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>241 → 245</td>
<td>0.392</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO:234</td>
<td>LUMO:235</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>232 → 235</td>
<td>232 → 235</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.161</td>
<td>-0.303</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>234 → 235</td>
<td>234 → 235</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.611</td>
<td>0.319</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HOMO:227</th>
<th>LUMO:228</th>
</tr>
</thead>
<tbody>
<tr>
<td>226 → 228</td>
<td>226 → 229</td>
</tr>
<tr>
<td>-0.225</td>
<td>-0.317</td>
</tr>
<tr>
<td>227 → 228</td>
<td>227 → 229</td>
</tr>
<tr>
<td>0.501</td>
<td>-0.288</td>
</tr>
<tr>
<td>227 → 228</td>
<td>227 → 229</td>
</tr>
<tr>
<td>0.136</td>
<td>0.245</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HOMO:220</th>
<th>LUMO:221</th>
</tr>
</thead>
<tbody>
<tr>
<td>219 → 221</td>
<td>219 → 222</td>
</tr>
<tr>
<td>0.316</td>
<td>0.375</td>
</tr>
<tr>
<td>220 → 221</td>
<td>220 → 222</td>
</tr>
<tr>
<td>-0.373</td>
<td>0.317</td>
</tr>
<tr>
<td>219 → 225</td>
<td>220 → 226</td>
</tr>
<tr>
<td>0.208</td>
<td>0.220</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HOMO:256</th>
<th>LUMO:257</th>
</tr>
</thead>
<tbody>
<tr>
<td>255 → 258</td>
<td>255 → 257</td>
</tr>
<tr>
<td>-0.112</td>
<td>0.680</td>
</tr>
<tr>
<td>255 → 258</td>
<td>255 → 258</td>
</tr>
<tr>
<td>0.135</td>
<td>0.253</td>
</tr>
<tr>
<td>256 → 262</td>
<td>256 → 263</td>
</tr>
<tr>
<td>-0.210</td>
<td>0.111</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HOMO:257</th>
<th>LUMO:258</th>
</tr>
</thead>
<tbody>
<tr>
<td>256 → 259</td>
<td>256 → 258</td>
</tr>
<tr>
<td>0.121</td>
<td>0.683</td>
</tr>
<tr>
<td>256 → 258</td>
<td>256 → 258</td>
</tr>
<tr>
<td>0.493</td>
<td>0.326</td>
</tr>
<tr>
<td>257 → 260</td>
<td>257 → 260</td>
</tr>
<tr>
<td>-0.256</td>
<td>-0.256</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HOMO:258</th>
<th>LUMO:259</th>
</tr>
</thead>
<tbody>
<tr>
<td>256 → 259</td>
<td>256 → 258</td>
</tr>
<tr>
<td>0.162</td>
<td>0.359</td>
</tr>
<tr>
<td>258 → 259</td>
<td>258 → 259</td>
</tr>
<tr>
<td>0.573</td>
<td>0.222</td>
</tr>
<tr>
<td>258 → 261</td>
<td>258 → 261</td>
</tr>
<tr>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>257</td>
<td>261</td>
</tr>
<tr>
<td>258</td>
<td>261</td>
</tr>
<tr>
<td>499.15nm</td>
<td>f=0.0650</td>
</tr>
<tr>
<td>HOMO:259</td>
<td>258</td>
</tr>
<tr>
<td>256</td>
<td>260</td>
</tr>
<tr>
<td>253</td>
<td>260</td>
</tr>
<tr>
<td>LUMO:260</td>
<td>259</td>
</tr>
<tr>
<td>257</td>
<td>260</td>
</tr>
<tr>
<td>254</td>
<td>260</td>
</tr>
<tr>
<td>259</td>
<td>261</td>
</tr>
<tr>
<td>257</td>
<td>261</td>
</tr>
<tr>
<td>255</td>
<td>260</td>
</tr>
<tr>
<td>258</td>
<td>261</td>
</tr>
<tr>
<td>257</td>
<td>261</td>
</tr>
<tr>
<td>258</td>
<td>261</td>
</tr>
<tr>
<td>259</td>
<td>262</td>
</tr>
<tr>
<td>445.2nm</td>
<td>f=0.1954</td>
</tr>
<tr>
<td>HOMO:260</td>
<td>257</td>
</tr>
<tr>
<td>257</td>
<td>261</td>
</tr>
<tr>
<td>251</td>
<td>261</td>
</tr>
<tr>
<td>LUMO:261</td>
<td>257</td>
</tr>
<tr>
<td>258</td>
<td>262</td>
</tr>
<tr>
<td>253</td>
<td>261</td>
</tr>
<tr>
<td>258</td>
<td>262</td>
</tr>
<tr>
<td>258</td>
<td>263</td>
</tr>
<tr>
<td>255</td>
<td>262</td>
</tr>
<tr>
<td>258</td>
<td>262</td>
</tr>
<tr>
<td>259</td>
<td>262</td>
</tr>
<tr>
<td>257</td>
<td>263</td>
</tr>
<tr>
<td>259</td>
<td>261</td>
</tr>
<tr>
<td>260</td>
<td>262</td>
</tr>
<tr>
<td>258</td>
<td>263</td>
</tr>
<tr>
<td>260</td>
<td>262</td>
</tr>
<tr>
<td>258</td>
<td>264</td>
</tr>
<tr>
<td>259</td>
<td>263</td>
</tr>
<tr>
<td>260</td>
<td>263</td>
</tr>
</tbody>
</table>
Fig. S1 Optimized structure of C$_{80}$H$_{30}$. Values in red are the dihedral angles (in degree) of the structure obtained with B3LYP/def-TZVP.
Fig. S2 Projected density of states (PDOS) of $C_{80}H_{30}$ and $C_{78}H_{80}$. 
**Fig. S3** The UV/Vis absorption spectra of C₈₀H₃₀ calculated with various functionals of B3LYP, Cam-B3LYP, PBE, PBE0, M06-2X and TPSSh.
Fig. S4 HOMO and LUMO orbitals of a–e.
Fig. S5 HOMO and LUMO orbitals of a'–e'.
Fig. S6 HOMO and LUMO contours of the model molecules shown in Fig. 4.