Electronic Supplementary Material (ESI) for Nanoscale.


**Supplementary Information**

# Free-energy predictions and absorption spectra calculations for supramolecular nanocarriers and their photoactive cargo

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*Details on the Electronic absorption spectra calculations*

The oscillator strengths were calculated for the monomer and stacked BODIPY chromophores. In particular, we clustered the BODIPY molecules belonging to each nanoparticle free-energy minima. Those resulted in two sets of clusters for the BODIPY monomer and one set of clusters for dimers and trimers.
Fifty singlet excited states were calculated at the TD-DFT framework with the B97-D[1] functional and 6-31G** basis sets using Gaussian 09 package.[2]
The oscillator strengths $f_{0n}$ are related to the transition dipole moment[3] by equation 5)

$$f^{0n} = \frac{2}{3}\omega^{0n}|\boldsymbol{\mu}^{0n}|^2 \qquad 5)$$

$\boldsymbol{\mu}_{0n}$ is the electric transition dipole moment associated with an electronic transition 0→ n and and $\omega^{0n}$ are the excitation energies for the specific transition.[3,4]

The calculations of the absorption spectra at a given wavelength, λ, were done assuming Gaussian bands with 600 $cm^{-1}$ full width at half-height (from 200 nm to 800 nm) for all transitions centered in a given excitation wavelength. A factor of $2.8710^4$ was applied in order to account for the conversion between oscillator strengths and the molar extinction coefficients.[5]

The values of the oscillator strengths calculated at TD-DFT level, within the B97-D functional19 and 6-31G** basis sets, are reported below.

**Table S1.** Oscillator strengths and relative wavelengths for the BODIPY monomer.

| | |
|---|---|
| **0.0586** | **526.64** |
| **0.4241** | **455.26** |
| **0.0032** | **431.44** |
| **0.0547** | **378.54** |
| **0.1477** | **364.89** |
| **0.0135** | **347.05** |
| **0.0050** | **326.44** |
| **0.0699** | **324.62** |
| **0.0049** | **301.71** |
| **0.0397** | **297.82** |
| **0.0192** | **295.97** |
| **0.0156** | **290.00** |
| **0.0054** | **264.59** |
| **0.0100** | **262.72** |
| **0.0086** | **260.77** |
| **0.0037** | **258.25** |
| **0.0010** | **256.08** |
| **0.0006** | **248.16** |
| **0.0012** | **242.32** |
| **0.0292** | **240.88** |
| **0.0534** | **239.78** |
| **0.0058** | **236.33** |
| **0.0036** | **235.43** |
| **0.0345** | **229.97** |
| **0.0161** | **228.69** |
| **0.0006** | **226.76** |
| **0.0156** | **224.69** |
| **0.0011** | **221.35** |
| **0.0003** | **219.68** |
| **0.0851** | **214.17** |
| **0.0090** | **210.71** |
| **0.0075** | **208.57** |
| **0.0106** | **207.99** |
| **0.0271** | **205.67** |
| **0.0053** | **205.09** |
| **0.0048** | **202.91** |
| **0.0009** | **201.21** |
| **0.0190** | **200.56** |
| **0.0014** | **198.54** |
| **0.0258** | **198.00** |
| **0.0673** | **197.43** |
| **0.0632** | **197.26** |
| **0.0025** | **196.18** |
| **0.0056** | **195.70** |
| **0.0055** | **194.69** |
| **0.0036** | **194.25** |
| **0.0012** | **193.86** |
| **0.1104** | **192.17** |
| **0.0433** | **191.36** |
| **0.0467** | **191.03** |

**Table S2.** Oscillator strengths and relative wavelengths for the second BODIPY monomer.

| | |
|---|---|
| **0.2853** | **461.75** |
| **0.1973** | **26.78** |
| **0.0024** | **376.76** |
| **0.0187** | **375.01** |
| **0.0025** | **303.97** |
| **0.0016** | **295.49** |
| **0.0068** | **287.46** |
| **0.0093** | **278.13** |
| **0.0013** | **273.58** |
| **0.0294** | **272.48** |
| **0.0003** | **265.68** |
| **0.0003** | **255.38** |
| **0.0040** | **253.50** |
| **0.0034** | **252.65** |
| **0.0020** | **249.79** |
| **0.0025** | **239.29** |
| **0.1592** | **237.25** |
| **0.0101** | **230.99** |
| **0.0375** | **228.92** |
| **0.0050** | **224.10** |
| **0.0007** | **222.56** |
| **0.0071** | **222.39** |
| **0.1013** | **220.52** |
| **0.0034** | **220.11** |
| **0.0088** | **216.89** |
| **0.0128** | **215.75** |
| **0.0027** | **214.31** |
| **0.0013** | **211.90** |
| **0.0079** | **211.01** |
| **0.0054** | **208.29** |
| **0.0002** | **207.69** |
| **0.0014** | **206.66** |
| **0.0189** | **203.77** |
| **0.0020** | **203.11** |
| **0.0043** | **201.86** |
| **0.0053** | **201.48** |
| **0.0155** | **199.75** |
| **0.0106** | **198.40** |
| **0.0106** | **198.30** |
| **0.0008** | **197.06** |
| **0.0078** | **196.44** |
| **0.0166** | **195.81** |
| **0.0125** | **194.97** |
| **0.0067** | **194.05** |
| **0.0510** | **193.82** |
| **0.0013** | **192.54** |
| **0.0061** | **192.03** |

**Table S3.** Oscillator strengths and relative wavelengths for the BODIPY dimer.

| | |
|---|---|
| **0.0014** | **788.63** |
| **0.0011** | **586.83** |
| **0.0009** | **562.11** |
| **0.0039** | **514.13** |
| **0.0238** | **492.59** |
| **0.0005** | **475.13** |
| **0.0116** | **463.75** |
| **0.0963** | **456.93** |
| **0.4864** | **427.41** |
| **0.0207** | **417.51** |
| **0.0058** | **413.97** |
| **0.3672** | **403.93** |
| **0.0104** | **399.22** |
| **0.0005** | **391.39** |
| **0.0003** | **380.31** |
| **0.0000** | **379.34** |
| **0.0005** | **371.80** |
| **0.0067** | **361.18** |
| **0.0090** | **358.39** |
| **0.0002** | **317.97** |
| **0.0000** | **316.21** |
| **0.0002** | **312.23** |
| **0.0005** | **311.99** |
| **0.0016** | **308.27** |
| **0.0030** | **305.70** |
| **0.0385** | **303.32** |
| **0.0596** | **302.58** |
| **0.0074** | **302.39** |
| **0.0001** | **302.15** |
| **0.0027** | **299.45** |
| **0.0038** | **297.47** |
| **0.0002** | **296.76** |
| **0.0005** | **295.66** |
| **0.0040** | **294.23** |
| **0.0349** | **293.49** |
| **0.0000** | **290.14** |
| **0.0020** | **288.50** |
| **0.0488** | **285.30** |
| **0.0001** | **283.58** |
| **0.0011** | **283.05** |

**Table S4.** Oscillator strengths and relative wavelengths for the BODIPY trimer.

| | |
|---|---|
| **0.0002** | **822.31** |
| **0.0011** | **772.46** |
| **0.0022** | **734.21** |
| **0.0024** | **660.64** |
| **0.0031** | **651.72** |
| **0.0003** | **610.69** |
| **0.0002** | **574.06** |
| **0.0001** | **567.27** |
| **0.0026** | **530.82** |
| **0.0022** | **526.26** |
| **0.0002** | **515.03** |
| **0.0007** | **507.78** |
| **0.0189** | **497.80** |
| **0.0283** | **481.77** |
| **0.0072** | **480.34** |
| **0.0313** | **477.10** |
| **0.0020** | **473.36** |
| **0.0354** | **472.51** |
| **0.0176** | **465.78** |
| **0.0028** | **455.91** |
| **0.1471** | **453.78** |
| **0.0232** | **447.67** |
| **0.6588** | **440.82** |
| **0.0205** | **438.93** |
| **0.0258** | **432.40** |
| **0.0020** | **420.87** |
| **0.0016** | **417.78** |
| **0.1538** | **415.14** |
| **0.0022** | **414.03** |
| **0.0066** | **412.70** |
| **0.0003** | **395.36** |
| **0.0099** | **389.89** |
| **0.0070** | **384.38** |
| **0.0000** | **384.15** |
| **0.0001** | **383.47** |
| **0.0026** | **380.32** |
| **0.0013** | **377.69** |
| **0.0554** | **376.07** |
| **0.0074** | **374.91** |
| **0.0169** | **369.98** |
| **0.0405** | **368.26** |
| **0.0021** | **364.22** |
| **0.0024** | **364.13** |
| **0.0545** | **361.22** |
| **0.0789** | **359.91** |
| **0.0295** | **359.43** |
| **0.1640** | **355.57** |
| **0.0039** | **353.37** |
| **0.0442** | **351.79** |
| **0.0093** | **349.57** |

**Table S5.** Coordinates of the first monomer BODIPY conformer.
Absolute energy= -1226.06069 Hartree

| | | | |
|---|---|---|---|
| **C** | **9.792** | **-20.332** | **25.231** |
| **H** | **10.175** | **-19.476** | **25.827** |
| **H** | **9.13** | **-20.084** | **24.374** |
| **H** | **9.323** | **-21.076** | **25.909** |
| **N** | **12.302** | **-20.962** | **25.143** |
| **C** | **11.045** | **-20.979** | **24.632** |
| **C** | **11.084** | **-21.728** | **23.462** |
| **C** | **12.362** | **-22.247** | **23.328** |
| **C** | **13.132** | **-21.708** | **24.326** |
| **C** | **9.951** | **-22.146** | **22.714** |
| **H** | **9.22** | **-21.31** | **22.726** |
| **H** | **10.342** | **-22.34** | **21.693** |
| **C** | **9.312** | **-23.517** | **23.132** |
| **H** | **10.071** | **-24.321** | **23.238** |
| **H** | **8.479** | **-23.868** | **22.487** |
| **H** | **8.834** | **-23.392** | **24.128** |
| **C** | **12.737** | **-23.278** | **22.228** |
| **H** | **13.351** | **-23.978** | **22.834** |
| **H** | **11.939** | **-23.93** | **21.812** |
| **H** | **13.332** | **-22.818** | **21.411** |
| **F** | **12.622** | **-18.997** | **26.495** |
| **F** | **12.004** | **-20.925** | **27.574** |
| **B** | **12.767** | **-20.318** | **26.578** |
| **C** | **14.568** | **-21.856** | **24.642** |
| **N** | **14.297** | **-20.649** | **26.725** |
| **C** | **15.085** | **-20.14** | **27.777** |
| **C** | **16.435** | **-20.433** | **27.479** |
| **C** | **16.454** | **-21.179** | **26.341** |
| **C** | **15.117** | **-21.294** | **25.82** |
| **C** | **14.53** | **-19.35** | **28.902** |
| **H** | **13.533** | **-19.747** | **29.189** |
| **H** | **14.42** | **-18.327** | **28.484** |
| **H** | **15.2** | **-19.545** | **29.767** |
| **C** | **17.524** | **-20.15** | **28.457** |
| **H** | **17.168** | **-19.186** | **28.881** |
| **H** | **18.499** | **-20.013** | **27.943** |
| **C** | **17.942** | **-21.22** | **29.4** |
| **H** | **18.28** | **-22.138** | **28.872** |
| **H** | **17.017** | **-21.483** | **29.955** |
| **H** | **18.681** | **-20.839** | **30.137** |
| **C** | **17.801** | **-21.599** | **25.786** |
| **H** | **18.707** | **-21.216** | **26.303** |
| **H** | **17.886** | **-21.304** | **24.718** |
| **H** | **17.921** | **-22.701** | **25.869** |
| **C** | **15.438** | **-22.369** | **23.757** |
| **C** | **15.681** | **-21.905** | **22.471** |
| **H** | **15.336** | **-20.941** | **22.127** |
| **C** | **16.481** | **-22.563** | **21.54** |
| **H** | **16.651** | **-22.189** | **20.541** |
| **C** | **17.03** | **-23.745** | **21.992** |
| **H** | **17.592** | **-24.225** | **21.204** |
| **C** | **16.088** | **-23.589** | **24.156** |
| **H** | **15.842** | **-23.971** | **25.135** |

| | | | |
|---|---|---|---|
| **C** | **16.819** | **-24.275** | **23.189** |
| **H** | **17.254** | **-25.244** | **23.383** |

**Table S6.** Coordinates of the second monomer BODIPY conformer.
Absolute energy= -1226.06941 Hartree

| | | | |
|---|---|---|---|
| **C** | **2.852334** | **-3.250029** | **-0.505486** |
| **H** | **3.493053** | **-3.519099** | **0.360118** |
| **H** | **2.034505** | **-4.000081** | **-0.453048** |
| **H** | **3.369696** | **-3.432731** | **-1.471525** |
| **7** | **1.177704** | **-1.343738** | **-0.216555** |
| **C** | **2.428966** | **-1.806703** | **-0.389742** |
| **C** | **3.318316** | **-0.711327** | **-0.321304** |
| **C** | **2.643598** | **0.382824** | **-0.163248** |
| **C** | **1.255335** | **0.027118** | **-0.151225** |
| **C** | **4.780781** | **-0.947280** | **-0.435206** |
| **H** | **4.978780** | **-1.865395** | **-1.029526** |
| **H** | **5.289056** | **-0.097829** | **-0.938911** |
| **C** | **5.367719** | **-1.141802** | **0.967308** |
| **H** | **6.454443** | **-1.305956** | **0.805312** |
| **H** | **4.923165** | **-2.057131** | **1.414864** |
| **H** | **5.081318** | **-0.315621** | **1.652288** |
| **C** | **3.377407** | **1.721778** | **0.092001** |
| **H** | **3.685274** | **2.185212** | **-0.869664** |
| **H** | **2.654044** | **2.404860** | **0.587033** |
| **H** | **4.239720** | **1.499222** | **0.755767** |
| **F** | **-0.401653** | **-3.238504** | **-0.957210** |
| **F** | **0.085518** | **-2.841153** | **1.340638** |
| **B** | **-0.064040** | **-2.221709** | **0.073124** |
| **C** | **0.075330** | **0.810753** | **-0.041219** |
| **N** | **-1.339629** | **-1.212801** | **0.130301** |
| **C** | **-2.652452** | **-1.515156** | **0.256706** |
| **C** | **-3.473913** | **-0.347762** | **0.136616** |
| **C** | **-2.572937** | **0.707119** | **0.038221** |
| **C** | **-1.229414** | **0.208025** | **0.026355** |
| **C** | **-3.256436** | **-2.905733** | **0.542861** |
| **H** | **-2.531331** | **-3.722273** | **0.333640** |
| **H** | **-4.155525** | **-3.202291** | **-0.037842** |
| **H** | **-3.362958** | **-2.847548** | **1.647655** |
| **C** | **-4.964134** | **-0.406812** | **0.254624** |
| **H** | **-5.273781** | **0.658520** | **0.195333** |
| **H** | **-5.241064** | **-0.667108** | **1.298622** |
| **C** | **-5.744115** | **-0.927623** | **-0.908402** |
| **H** | **-5.346775** | **-0.328296** | **-1.754770** |
| **H** | **-6.828231** | **-0.705513** | **-0.805906** |
| **H** | **-5.586134** | **-2.012863** | **-1.085871** |
| **C** | **-3.055786** | **2.141123** | **-0.179184** |
| **H** | **-3.988354** | **2.205012** | **-0.779975** |
| **H** | **-2.293463** | **2.853197** | **-0.561938** |
| **H** | **-3.242609** | **2.475567** | **0.864072** |
| **C** | **0.242259** | **2.157917** | **0.006173** |
| **C** | **0.824636** | **2.872341** | **-1.041099** |
| **H** | **1.320325** | **2.263697** | **-1.783620** |
| **C** | **0.886028** | **4.290640** | **-0.992337** |
| **H** | **1.396336** | **4.805860** | **-1.792519** |

| | | | |
|---|---|---|---|
| C | 0.289676 | 4.918236 | 0.084869 |
| H | 0.431472 | 5.977003 | 0.242229 |
| C | -0.382009 | 2.803147 | 1.024526 |
| H | -0.714579 | 2.193363 | 1.851463 |
| C | -0.288012 | 4.180729 | 1.080216 |
| H | -0.826553 | 4.710307 | 1.851877 |

**Table S7.** Coordinates of the stacked BODIPY dimer.
Absolute energy= -2452.17921 Hartree

| | | | |
|---|---|---|---|
| C | -5.904237 | -1.357033 | -1.912119 |
| H | -6.860510 | -0.921805 | -1.551922 |
| H | -5.579882 | -0.658866 | -2.713137 |
| H | -6.086311 | -2.305875 | -2.462069 |
| N | -4.092206 | -0.433321 | -0.332121 |
| C | -4.879723 | -1.486118 | -0.762734 |
| C | -4.413022 | -2.613980 | -0.065333 |
| C | -3.501015 | -2.198013 | 0.862693 |
| C | -3.261440 | -0.828340 | 0.671184 |
| C | -4.977962 | -3.925986 | -0.300155 |
| H | -5.000624 | -4.412182 | 0.698019 |
| H | -6.026991 | -3.798330 | -0.643527 |
| C | -4.062696 | -4.624784 | -1.266663 |
| H | -2.979149 | -4.587538 | -1.022392 |
| H | -4.138880 | -4.146867 | -2.266222 |
| H | -4.444464 | -5.667894 | -1.271094 |
| C | -2.821179 | -3.102614 | 1.904003 |
| H | -3.136942 | -4.163947 | 1.814008 |
| H | -1.728344 | -2.999858 | 1.734904 |
| H | -3.150060 | -2.664543 | 2.870939 |
| F | -4.085486 | 1.241511 | -2.257313 |
| F | -5.468719 | 1.543342 | -0.505024 |
| B | -4.210610 | 1.029304 | -0.875158 |
| C | -2.376883 | 0.124663 | 1.338772 |
| N | -3.171846 | 1.895076 | -0.008011 |
| C | -2.995654 | 3.228270 | -0.185669 |
| C | -1.983491 | 3.657360 | 0.673259 |
| C | -1.525139 | 2.586988 | 1.329792 |
| C | -2.328660 | 1.495526 | 0.968569 |
| C | -3.859879 | 4.144226 | -1.004393 |
| H | -3.639368 | 5.185260 | -0.683791 |
| H | -4.932526 | 3.884654 | -0.884600 |
| H | -3.627346 | 4.126374 | -2.090714 |
| C | -1.321701 | 4.968525 | 0.600229 |
| H | -1.474844 | 5.242525 | -0.465511 |
| H | -0.239820 | 4.907480 | 0.843403 |
| C | -1.839509 | 6.011003 | 1.600471 |
| H | -1.146627 | 6.849121 | 1.825643 |
| H | -2.022136 | 5.494872 | 2.566657 |
| H | -2.770326 | 6.463623 | 1.194219 |
| C | -0.495541 | 2.689448 | 2.397942 |
| H | -0.117210 | 1.682329 | 2.674674 |
| H | -1.021958 | 3.057452 | 3.304052 |
| H | 0.378655 | 3.331499 | 2.155848 |
| C | -1.629105 | -0.249436 | 2.396880 |

| | | | |
|---|---|---|---|
| C | -0.347087 | -0.762202 | 2.172718 |
| H | 0.096445 | -0.770089 | 1.188291 |
| C | 0.340660 | -1.260812 | 3.239271 |
| H | 1.264786 | -1.808351 | 3.124933 |
| C | -0.095632 | -1.214577 | 4.540631 |
| H | 0.510742 | -1.562949 | 5.363510 |
| C | -2.110151 | -0.248635 | 3.693903 |
| H | -3.039936 | 0.279037 | 3.848567 |
| C | -1.296257 | -0.615084 | 4.791987 |
| H | -1.641505 | -0.439500 | 5.799302 |
| C | 0.672708 | 3.234817 | -1.963943 |
| H | 0.924453 | 4.282907 | -2.231809 |
| H | 0.268624 | 2.645104 | -2.814593 |
| H | -0.158750 | 3.227178 | -1.226887 |
| N | 1.964056 | 1.161044 | -1.185048 |
| C | 1.927355 | 2.568308 | -1.282985 |
| C | 3.113576 | 3.040685 | -0.749275 |
| C | 3.909480 | 1.986516 | -0.390905 |
| C | 3.183239 | 0.789472 | -0.590929 |
| C | 3.413968 | 4.469156 | -0.751794 |
| H | 2.407360 | 4.891413 | -0.544908 |
| H | 4.020374 | 4.744868 | 0.136211 |
| C | 4.042560 | 5.119161 | -2.000535 |
| H | 5.063575 | 4.681782 | -2.027538 |
| H | 4.048450 | 6.213219 | -1.806648 |
| H | 3.482320 | 4.820283 | -2.911280 |
| C | 5.251293 | 2.227846 | 0.253379 |
| H | 5.889422 | 1.336070 | 0.078768 |
| H | 5.634901 | 3.182890 | -0.165985 |
| H | 4.970087 | 2.267801 | 1.327517 |
| 9 | -0.396721 | 0.272748 | -1.329861 |
| 9 | 1.070755 | 0.432826 | -3.178344 |
| 5 | 0.938983 | 0.127944 | -1.791572 |
| C | 3.489075 | -0.559847 | -0.345392 |
| N | 1.384709 | -1.330198 | -1.483012 |
| C | 0.794113 | -2.518551 | -1.737137 |
| C | 1.593830 | -3.565458 | -1.245880 |
| C | 2.696064 | -3.027955 | -0.629406 |
| C | 2.660774 | -1.620404 | -0.769804 |
| C | -0.552128 | -2.572574 | -2.457218 |
| H | -1.387327 | -2.263790 | -1.792237 |
| H | -0.921145 | -3.519783 | -2.906775 |
| H | -0.460299 | -1.751176 | -3.199678 |
| C | 1.079218 | -4.892833 | -1.342420 |
| H | 1.948311 | -5.583203 | -1.395140 |
| H | 0.582781 | -4.998480 | -2.330777 |
| C | 0.166638 | -5.316267 | -0.240742 |
| H | -0.683473 | -4.603572 | -0.191668 |
| H | 0.718796 | -5.201096 | 0.717524 |
| H | -0.053386 | -6.396037 | -0.384039 |
| C | 3.748510 | -3.932732 | -0.021801 |
| H | 3.115497 | -4.765175 | 0.353981 |
| H | 4.163941 | -3.375147 | 0.844246 |
| H | 4.576940 | -4.309351 | -0.659605 |
| C | 4.731527 | -0.894341 | 0.172881 |
| C | 5.037591 | -0.597877 | 1.460885 |
| H | 4.396273 | 0.009731 | 2.082375 |

| | | | |
|---|---|---|---|
| **C** | **6.242234** | **-0.885181** | **2.007095** |
| **H** | **6.343210** | **-0.699048** | **3.065807** |
| **C** | **7.208326** | **-1.506476** | **1.214203** |
| **H** | **8.131714** | **-1.845335** | **1.661250** |
| **C** | **5.670847** | **-1.563425** | **-0.584649** |
| **H** | **5.429675** | **-1.770382** | **-1.616483** |
| **C** | **6.954714** | **-1.843821** | **-0.108652** |
| **H** | **7.688239** | **-2.405267** | **-0.669043** |

**Table S8.** Coordinates of the stacked BODIPY trimer.
Absolute energy= -3678.27120 Hartree

| | | | |
|---|---|---|---|
| **C** | **7.616597** | **-2.774530** | **-2.561910** |
| **H** | **7.209910** | **-2.323643** | **-3.492604** |
| **H** | **8.696911** | **-2.549861** | **-2.434908** |
| **H** | **7.481128** | **-3.875519** | **-2.615445** |
| **N** | **6.678232** | **-1.069075** | **-0.899169** |
| **C** | **6.966081** | **-2.379718** | **-1.273149** |
| **C** | **6.495835** | **-3.258712** | **-0.312427** |
| **C** | **5.915966** | **-2.545440** | **0.696359** |
| **C** | **6.043529** | **-1.127611** | **0.299761** |
| **C** | **6.959348** | **-4.634956** | **-0.231385** |
| **H** | **7.958728** | **-4.743324** | **-0.703619** |
| **H** | **7.256847** | **-5.081139** | **0.741959** |
| **C** | **6.037239** | **-5.619613** | **-0.841354** |
| **H** | **5.584181** | **-5.300577** | **-1.804451** |
| **H** | **5.222215** | **-5.755292** | **-0.099155** |
| **H** | **6.536917** | **-6.568108** | **-1.133441** |
| **C** | **5.080925** | **-3.190015** | **1.718268** |
| **H** | **5.636520** | **-3.241986** | **2.679647** |
| **H** | **4.146956** | **-2.600486** | **1.835804** |
| **H** | **4.786466** | **-4.211802** | **1.397323** |
| **F** | **8.185024** | **0.354596** | **-2.129863** |
| **F** | **6.066424** | **-0.070109** | **-2.977926** |
| **B** | **6.782898** | **0.181241** | **-1.877127** |
| **C** | **5.589407** | **0.054493** | **0.922921** |
| **N** | **6.185702** | **1.329383** | **-1.058731** |
| **C** | **6.131083** | **2.619976** | **-1.449457** |
| **C** | **5.599304** | **3.370203** | **-0.446980** |
| **C** | **5.391609** | **2.564165** | **0.611869** |
| **C** | **5.711634** | **1.296025** | **0.274824** |
| **C** | **6.477913** | **3.091196** | **-2.863225** |
| **H** | **5.704567** | **2.953845** | **-3.648128** |
| **H** | **7.338014** | **2.477608** | **-3.206393** |
| **H** | **6.663880** | **4.186983** | **-2.873228** |
| **C** | **5.538513** | **4.902858** | **-0.554528** |
| **H** | **6.572024** | **5.150734** | **-0.878224** |
| **H** | **5.394413** | **5.354527** | **0.450383** |
| **C** | **4.488926** | **5.455537** | **-1.474301** |
| **H** | **4.668913** | **6.531392** | **-1.682475** |
| **H** | **3.566628** | **5.290466** | **-0.877768** |
| **H** | **4.480252** | **4.874748** | **-2.421876** |
| **C** | **5.290993** | **3.132183** | **1.975619** |
| **H** | **4.268062** | **3.475746** | **2.238109** |
| **H** | **5.883194** | **4.071469** | **1.937754** |

| | | | |
|---|---|---|---|
| H | 5.643577 | 2.561035 | 2.860835 |
| C | 5.030179 | -0.046251 | 2.167161 |
| C | 5.694068 | -0.543975 | 3.233690 |
| H | 6.717427 | -0.871942 | 3.127809 |
| C | 5.133178 | -0.585617 | 4.503311 |
| H | 5.760637 | -0.828604 | 5.347554 |
| C | 3.845871 | -0.107092 | 4.666360 |
| H | 3.491978 | -0.138965 | 5.686852 |
| C | 3.732163 | 0.408552 | 2.402712 |
| H | 3.189630 | 0.780686 | 1.545561 |
| C | 3.101923 | 0.359790 | 3.603996 |
| H | 2.199757 | 0.918908 | 3.801519 |
| C | 2.789314 | -1.566446 | -1.233947 |
| H | 2.982973 | -0.511448 | -1.520785 |
| H | 3.706919 | -2.085022 | -0.883527 |
| H | 2.412888 | -2.207294 | -2.059375 |
| N | 0.896511 | -0.389669 | 0.012316 |
| C | 1.706013 | -1.516577 | -0.192716 |
| C | 1.145551 | -2.527272 | 0.624820 |
| C | 0.076077 | -2.064648 | 1.372466 |
| C | -0.070790 | -0.654292 | 1.062525 |
| C | 1.641076 | -3.913072 | 0.551027 |
| H | 2.616829 | -4.035378 | 0.034054 |
| H | 1.773551 | -4.441723 | 1.519549 |
| C | 0.694304 | -4.921775 | -0.150657 |
| H | 0.982730 | -5.933530 | 0.208188 |
| H | 0.698312 | -4.935530 | -1.261330 |
| H | -0.351043 | -4.730563 | 0.172230 |
| C | -0.768964 | -2.854086 | 2.310494 |
| H | -0.826512 | -2.412938 | 3.328788 |
| H | -1.806068 | -2.931755 | 1.918961 |
| H | -0.238350 | -3.825850 | 2.229688 |
| 9 | 2.178936 | 1.673103 | -0.447851 |
| 9 | 0.705404 | 0.853350 | -2.072926 |
| 5 | 0.950313 | 1.069883 | -0.676799 |
| C | -1.009622 | 0.384930 | 1.489038 |
| N | -0.169609 | 2.060738 | -0.068439 |
| C | -0.324890 | 3.412409 | -0.326909 |
| C | -1.393481 | 3.876336 | 0.475678 |
| C | -1.744760 | 2.840506 | 1.350549 |
| C | -1.029817 | 1.679081 | 0.971957 |
| C | 0.685192 | 4.208197 | -1.105093 |
| H | 0.437931 | 5.288191 | -1.017337 |
| H | 0.753887 | 3.877471 | -2.164188 |
| H | 1.694690 | 4.131072 | -0.648053 |
| C | -1.823432 | 5.315747 | 0.468881 |
| H | -2.892544 | 5.277223 | 0.768219 |
| H | -1.837725 | 5.823743 | -0.519453 |
| C | -1.143602 | 6.318926 | 1.385318 |
| H | -0.056821 | 6.301486 | 1.157408 |
| H | -1.286716 | 5.983992 | 2.435273 |
| H | -1.593604 | 7.334475 | 1.341315 |
| C | -2.641006 | 3.094944 | 2.516066 |
| H | -2.479468 | 4.156120 | 2.804431 |
| H | -2.376346 | 2.455619 | 3.385491 |
| H | -3.692442 | 2.878367 | 2.231457 |
| C | -1.820355 | 0.029053 | 2.492972 |

| | | | |
|---|---|---|---|
| C | -1.340703 | -0.161434 | 3.831965 |
| H | -0.294433 | -0.101187 | 4.094935 |
| C | -2.210983 | -0.439562 | 4.821398 |
| H | -1.794953 | -0.592235 | 5.806246 |
| C | -3.586677 | -0.588346 | 4.555791 |
| H | -4.187851 | -0.831324 | 5.420011 |
| C | -3.170995 | -0.130090 | 2.254310 |
| H | -3.571089 | -0.160458 | 1.251595 |
| C | -4.039945 | -0.375276 | 3.311323 |
| H | -4.988247 | -0.757542 | 2.965172 |
| C | -2.097687 | -3.133880 | -2.709347 |
| H | -2.229528 | -2.694774 | -3.720604 |
| H | -1.301427 | -2.572953 | -2.175258 |
| H | -1.773741 | -4.192088 | -2.805696 |
| N | -3.938505 | -1.705839 | -1.708605 |
| C | -3.389579 | -2.941933 | -1.879523 |
| C | -4.262131 | -3.862830 | -1.322256 |
| C | -5.342582 | -3.198811 | -0.813569 |
| C | -5.087692 | -1.827418 | -1.020889 |
| C | -4.039321 | -5.287154 | -1.283548 |
| H | -2.943781 | -5.404306 | -1.146320 |
| H | -4.597674 | -5.796499 | -0.469287 |
| C | -4.376800 | -5.919348 | -2.593452 |
| H | -3.729400 | -5.451019 | -3.365471 |
| H | -5.439381 | -5.664982 | -2.793672 |
| H | -4.185938 | -7.009757 | -2.505105 |
| C | -6.550431 | -3.935835 | -0.250177 |
| H | -7.445606 | -3.462859 | -0.707829 |
| H | -6.528606 | -4.961403 | -0.676822 |
| H | -6.531354 | -3.922787 | 0.861289 |
| 9 | -2.044340 | -0.339388 | -1.535603 |
| 9 | -3.083115 | -0.203515 | -3.626314 |
| 5 | -3.300173 | -0.325876 | -2.201534 |
| C | -5.898092 | -0.703465 | -0.648521 |
| N | -4.262639 | 0.844464 | -1.666303 |
| C | -4.183062 | 2.219846 | -1.928199 |
| C | -5.267673 | 2.850186 | -1.335922 |
| C | -6.031408 | 1.930545 | -0.744667 |
| C | -5.483085 | 0.622253 | -1.022908 |
| C | -2.958170 | 2.892517 | -2.599947 |
| H | -2.082678 | 2.228932 | -2.764695 |
| H | -2.664305 | 3.805682 | -2.040528 |
| H | -3.445410 | 3.194458 | -3.551715 |
| C | -5.450862 | 4.303049 | -1.273014 |
| H | -4.484517 | 4.778592 | -1.545934 |
| H | -5.542225 | 4.665064 | -0.226091 |
| C | -6.477973 | 4.890353 | -2.210952 |
| H | -6.457947 | 5.999801 | -2.156309 |
| H | -7.487457 | 4.645272 | -1.818670 |
| H | -6.473725 | 4.543618 | -3.267012 |
| C | -7.186242 | 2.331715 | 0.109045 |
| H | -8.090796 | 2.502789 | -0.513555 |
| H | -6.893046 | 3.254496 | 0.653594 |
| H | -7.300251 | 1.596077 | 0.933271 |
| C | -7.049307 | -0.882072 | 0.044912 |
| C | -7.179944 | -1.474930 | 1.311661 |
| H | -6.346198 | -1.901569 | 1.850997 |

| | | | |
|---|---|---|---|
| **C** | **-8.382980** | **-1.575448** | **1.924826** |
| **H** | **-8.492566** | **-2.101786** | **2.860999** |
| **C** | **-9.500223** | **-1.156663** | **1.252593** |
| **H** | **-10.469952** | **-1.204356** | **1.723992** |
| **C** | **-8.249679** | **-0.552688** | **-0.685569** |
| **H** | **-8.268413** | **-0.292916** | **-1.734216** |
| **C** | **-9.422406** | **-0.559422** | **-0.002291** |
| **H** | **-10.343083** | **-0.163803** | **-0.405588** |

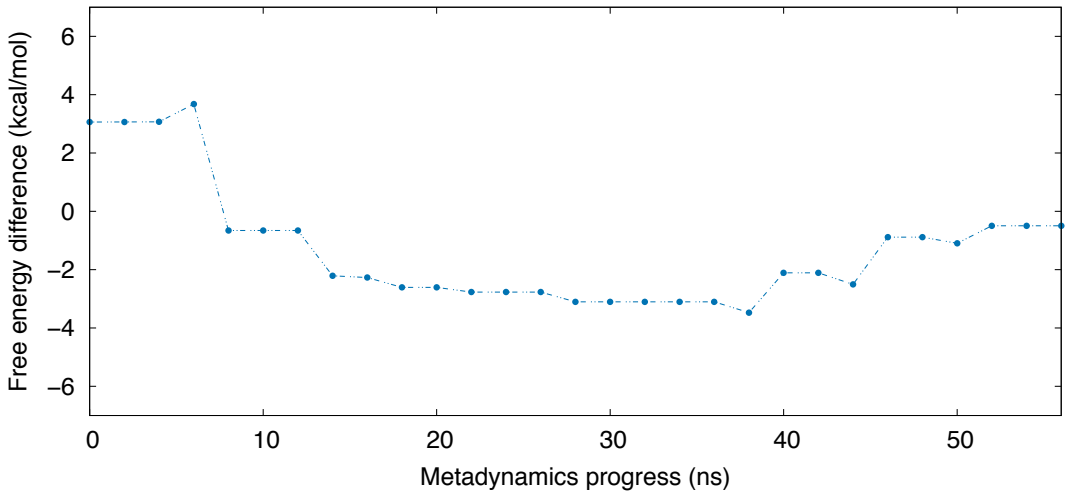


**Figure S1.** Free-energy convergence estimated from the free-energy difference between the four-sized nanoparticle free-energy basin and the six-sized nanoparticle free energy basin as a function of the metadynamics progress.

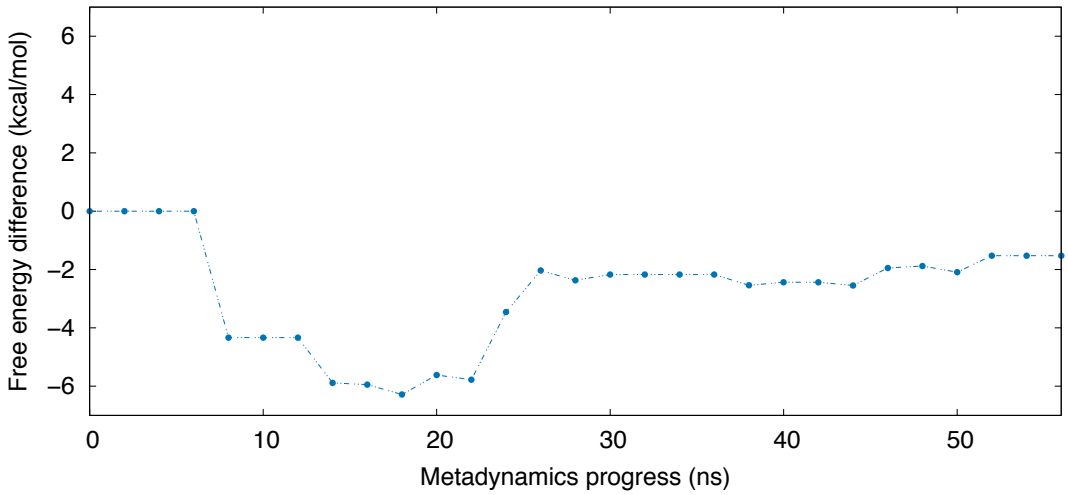


**Figure S2.** Free-energy convergence estimated from the free-energy difference between the four-sized free-energy nanoparticle basin and the five-sized nanoparticle free energy basin as a function of the metadynamics progress.

**References**


1. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
2. Gaussian 09, Revision D.01, M. J. Frisch *et al.*, Gaussian, Inc., Wallingford CT, 2009.
3. F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Voegtle and S. Grimme, *J. Am. Chem. Soc.*, 2000, **122**, 1717.
4. R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454.
5. S. Grimme, *Rev. Comput. Chem.*, 2004, **20**, 153.