Stereospecific Synthesis and Photophysical Properties of Propeller-Shaped C90H48 PAH

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Highly twisted large PAHs offer, in addition to physical properties, a feature of chirality, which results in non-super imposable mirror-image structures of these compounds that can be resolved into optically active enantiomers. This process, however, is cumbersome, which largely restricts the available quantity of materials in optically active form and represents a great hurdle for their applications. Herein, we have synthesized an enantiomerically pure propeller-shaped PAH, $C_{90}H_{48}$, possessing three [7]helicene and three [5]helicene subunits. This compound can be obtained in gram quantities in a straight-forward manner. The photophysical and chiroptical properties were investigated using UV–vis absorption and emission, optical rotation and circular dichroism spectroscopy, supported by DFT calculations. The non-linear optical properties were investigated by two-photon absorption measurements using linearly and circularly polarized light. The extremely twisted structure and packing of the homochiral compound were investigated by single crystal X-ray diffraction analysis.

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Stereospecific synthesis and photophysical properties of propeller-shaped C$_{90}$H$_{48}$ PAH

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ABSTRACT:
Highly twisted large polycyclic aromatic hydrocarbons (PAHs) offer, in addition to physical properties, a feature of chirality, which results in non-super imposable mirror-image structures of these compounds that can be resolved into optically active enantiomers. This process, however, is cumbersome, which largely restricts the available quantity of materials in optically active form and represents a great hurdle for their applications. Herein, we have synthesized an enantiomerically pure propeller-shaped PAH, C₉₀H₄₈, possessing three [7]helicene and three [5]helicene subunits. This compound can be obtained in gram quantities in a straight-forward manner. The photophysical and chiroptical properties were investigated using UV–vis absorption and emission, optical rotation and circular dichroism spectroscopy, supported by DFT calculations. The non-linear optical properties were investigated by two-photon absorption measurements using linearly and circularly polarized light. The extremely twisted structure and packing of the homochiral compound were investigated by single crystal X-ray diffraction analysis.

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- stereospecific synthesis
- enantiomerically pure
- gram quantities
- chiroptical properties
- nonlinear optical properties
INTRODUCTION

Polycyclic aromatic hydrocarbons\(^1\) (PAHs) with multiple helicene sub-structures are of special interest for synthetic and materials chemists owing to their unique chiroptical and non-linear optical properties, structural beauty, and synthetic challenge.\(^2\) These interests have been fueled by their potential applications\(^3\) as circularly polarized light (CPL) emitters in OLEDs\(^4\), CPL responsive OFETs\(^5\), spin filters,\(^6\) and photoswitches\(^7\). In the past few years, synthetic organic chemists in this field have witnessed a great progress.\(^8\) PAHs with double\(^9\), triple\(^10\), quadruple\(^11\), quintuple\(^12\), and sextuple\(^13\) helicene subunits ([4]\(^{10a}\), [5]\(^{9d}\), [10c], [13f], [13g], [14], [6]\(^{9e}\), [11b], [12b], [7]\(^{9a}\), [9c], [13b], [13c], [13e], or [9]\(^{13a}\) helicenes) have been achieved. Despite of this enormous synthetic success, however, the studies of this class of compounds are still limited by separation of their enantiomerically pure forms in minute quantities and investigation of their chiroptical properties by circular dichroism (CD) and circularly polarized luminescence spectroscopy, and these compounds have rarely been used for any application purpose.

The non-stereoselective/stereospecific synthesis of PAHs with \(m\) number of helicene sub-structures can possibly yield \(\leq 2^m\) stereoisomers depending on the symmetry and stereodynamics of the molecule. The asymmetric synthesis of PAHs with multiple helices is yet to be developed.\(^2b\) By employing the non-asymmetric synthesis, the obtained mixture of enantiomers is usually separated with the help of HPLC employing chiral stationary phase columns. These are very expensive and their cost increases dramatically on moving from the analytical to semi-preparative and preparative scale. Additionally, there is no universal column that could be used for the same class of molecules. Often even for the compounds with a very similar structure, the baseline separation cannot be achieved with the same column. Moreover, the large structure and limited solubility makes the separation of such compounds into enantiomers cumbersome. This issue can be considered a great hurdle in transforming these structural beauties into applications.
Herein, we report the bottom-up stereospecific synthesis of a novel enantiomerically pure propeller-shaped molecule possessing six helicenes sub-structures comprising three [7]helicene and three [5]helicene subunits. The synthesized compound is fully characterized by 1D and 2D NMR, UV–vis absorption and emission, optical rotation (OR) and circular dichroism (CD) spectroscopy, MALDI-TOF mass spectrometry, and single crystal X-ray diffraction. The nonlinear optical properties are investigated by two-photon absorption experiments using linearly and circularly polarized light.

RESULTS AND DISCUSSION

Molecular design

**Figure 1.** (a) Kamikawa’s and (b) Gingras’ synthesis of sextuple helicenes obtained as the thermodynamically most stable single pair of enantiomers out of 20 possible stereoisomers.
One of the best studied examples of multi-helicene compounds is sextuplet helicene 1 reported by group of Kamikawa and Gingras independently at the same time (Figure 1). The six helicene subunits in 1 give rise to 20 possible stereoisomers, namely, 10 pairs of enantiomers. Interestingly, Kamikawa’s palladium-catalyzed room-temperature synthesis afforded exclusively diastereomer 1a, which upon heating for only three hours at 100 °C transformed into diastereomer 1b. Gingras’ nickel-mediated Yamamoto type reaction at 120 °C resulted in a mixture of diastereomers, which were also transformed exclusively into diastereomer 1b when heated at the same temperature for 30 min. The sole formation of diastereomer 1b at higher temperature can be attributed to its much higher thermodynamic stability in comparison to the other stereoisomers and labile configuration of [5]helicenes (ΔG‡ (298 K) = 24.1 kcal/mol). Preferred formation of the thermodynamically most stable stereoisomers was also observed in the course of the synthesis of other multi-helicene compounds at higher temperatures. Despite the formation of a single diastereomer, the challenge to resolve its enantiomers by HPLC with chiral stationary phase columns remains. This challenge has already been faced by Kamikawa, who resolved isomer 1b into enantiomers. The attempts to resolve 1a were not successful.

Recently, we investigated the trend of configurational stabilities among [n]helicenes (n = 4–11) and found an exponential increase in configurational stability with increasing the number of ortho-fused rings (n). [n]Helicenes with n > 6 are configurationally stable even at elevated temperatures. If in Gingras’ synthesis of 1b the 7,8-dibromo[5]helicene is replaced by configurationally stable and enantiomerically pure 9,10-dibromo[7]helicene (M or P), one should obtain sextuple helicene as a single enantiomer benefiting from the configurational stability of [7]helicene and flexibility of [5]helicene.
Synthesis and Characterization.

Scheme 1. (a) Stereospecific synthesis of enantiopure PAH 3 and (b) relative energies of the four possible diastereomers.

The enantiopure 9,10-dibromo[7]helicene was synthesized\textsuperscript{17} from the optically pure 1,1'-bi-(2-phenanthrol) in four steps with retention of configuration and optical purity. The latter compound can be accessed in an enantiopure form by asymmetric catalysis or with the help of chiral auxiliaries.\textsuperscript{18} To our delight, the nickel-mediated Yamamoto type [2+2+2] cyclotrimerization of (M)-9,10-dibromo[7]helicene (M-2) at 110 °C formed exclusively diastereomer (M,M,M,P,P,P)-3 in enantiomerically pure form (Scheme 1a) in 57 % yield. At this temperature, the [7]helicene subunit has a half-life for enantiomerization of $1.8 \times 10^9$ min.$^{15, 19}$ therefore, [7]helicene subunits do not undergo enantiomerization under these conditions. On the other hand, the newly formed [5]helicene subunits are still configurationally
flexible. Restricting the configurational resilience to only [5]helicenes limits the number of theoretically possible stereoisomers to four diastereomers, C-2 symmetric \((M,M,M,P,P,M)\) and \((M,M,M,P,M,M)\), and D-3 symmetric \((M,M,M,P,P,P)\) and \((M,M,M,M,M,M)\), unlike the 20 stereoisomers of 1. The exclusive formation of diastereomer \((M,M,M,P,P,P)\)-3 can be rationalized considering the relative thermodynamic stability of each stereoisomer (Scheme 1b). \((M,M,M,P,P,P)\)-3 is 15 kcal/mol lower in energy than the energetically adjacent stereoisomer \((M,M,M,P,P,M)\)-3. The energy difference between the thermodynamically most and least stable stereoisomer is 23 kcal/mol. Compound \((M,M,M,P,P,P)\)-3 can be easily synthesized in gram quantities and purified by routine silica gel column chromatography using petrol ether/toluene (1/1) as an eluent. The structure and purity of \((M,M,M,P,P,P)\)-3 could be unambiguously confirmed by 1D and 2D NMR spectroscopy and MALDI-TOF mass spectrometry.

![Figure 2. \(^1\)H NMR spectrum of \((M,M,M,P,P,P)\)-3 in CDCl\(_3\) at 298 K and assigned corresponding proton signals (residual solvent CHCl\(_3\) peak and satellite peaks are marked with](image-url)

an asterisk). Top left: experimental and simulated high-resolution MALDI mass isotopic pattern.

Each proton and carbon signal could be assigned with the aid of 2D NMR (COSY, NOESY, HMBC, and HSQC) experiments, which confirmed the structure of compound 3 (Figure S5–S8). The assignment of proton resonances is shown in Figure 2. The downfield shift of proton $h$ is due to the steric interaction in the fjord region of the helicene subunits, which is in consistence with that of [5]helicenes. Moreover, the presence of only eight signals indicate the higher $D_{3}$ symmetry of the molecule. At this point, the formation of $C_{2}$ symmetric isomers could be completely ruled out. Later, the single crystal X-ray analysis, OR, and CD spectroscopic data supported by (TD)-DFT calculation (vide-infra) conferred the structure to that of diastereomer $(M,M,M,P,P,P)-3$. The other enantiomer $(P,P,P,M,M,M)-3$ is obtained when the synthesis is started with enantiopure $(P)-9,10$-dibromo[7]helicene instead of the $(M)$-isomer.

**Figure 3.** Solid-state structure of $(M,M,M,P,P,P)-3$. Thermal ellipsoids are shown at the 50% probability level.
Single crystals of homochiral molecule (M,M,M,P,P,P)-3 were grown by a slow diffusion of hexane into a solution of 3 in toluene in an NMR tube. Compound 3 crystallizes in the chiral orthorhombic $P_{2_1}2_12_1$ space group (Figure 3). Similar to 1b, compound 3 also exhibits an extremely twisted structure and highly deformed benzene ring (B), which adopts twisted chair-like conformation. The crystal packing analysis revealed the slipped stacking arrangement of molecules held together by $\pi$–$\pi$ interactions (Figure S9).

**UV–Vis Spectroscopy.**

The UV–vis absorption and emission spectra of (M,M,M,P,P,P)-3 in chloroform, THF, and toluene are nearly identical, indicating no solvent effect on the excited state of the molecule (Figure S1). Compound 3 exhibited similar photophysical properties as 1b. The calculated optical energy gap of 3, 2.33 eV, from the onset of absorption spectrum (535 nm) is marginally smaller than that of 1b (2.38 eV). The absorption maximum in the visible range is, however, red-shifted by 50 eV with nearly double molar absorptivity (Figure 4, $\lambda_{\text{max}} = 418$ nm, $\varepsilon = 77,276$ M$^{-1}$ cm$^{-1}$). To get an insight into electronic transitions, the absorption UV–vis spectrum was analyzed with the aid of TD-DFT at UB3LYP/6-31G(d,p) level. The calculated absorption spectrum is shifted by 41 eV compared to experimental spectrum. The significant extension of $\pi$-conjugation upon replacing three [5]helicene units with three [7]helicene units resulted in only a small decrease of the calculated HOMO–LUMO energy gap (3.14 eV for 3 and 3.33 eV for 1b). This trend is also observed in naked carbo[n]helicenes. Interestingly, the HOMO and LUMO frontier molecular orbitals are energetically degenerate with the HOMO–1 and LUMO+1 orbitals, respectively. While the maximum absorption (447 nm, oscillator strength ($f = 1.05$) is mainly stemming from the HOMO–1→LUMO, HOMO→LUMO+1, HOMO–1→LUMO+1, and HOMO→LUMO transitions, the lowest energy absorption (473 nm, $f = 0.10$) is mainly from the HOMO–1→LUMO, HOMO–1→LUMO+1, and HOMO→LUMO transitions. Like the absorption spectrum, the emission spectrum of 3 is also
red-shifted by 41 eV compared to 1b with similar fluorescence lifetime (5.22 ns) and slightly enhanced quantum yield (7.3%).

![Figure 4. Measured UV–vis absorption (blue line, \(c = 1.4 \times 10^{-5} \) M) and emission (red line, \(c = 1.4 \times 10^{-5} \) M, \(\lambda_{ex} = 410 \) nm) spectra of \((M,M,M,P,P,P)-3\) in chloroform. Calculated (vertical gray lines) UV–vis spectrum (TD-DFT/UB3LYP/6-31G(d,p)) Note: calculated spectrum shifted by 41 eV.

OR and CD spectroscopy.

Another interesting feature of PAHs with multiple \([n]\)helicene units is OR value. \((M,M,M,P,P,P)-1b\) exhibited specific OR (\([\alpha]_{D}^{22}\)) of +495°, which is much smaller than that of \((M)-[5]\)helicene\(^{21}\) (−1670°) and could be elucidated from the presence of three \(P\) and three \(M\) helicene units. Moreover, the observed net positive value of optical rotation was attributed to the more pronounced helical twist of internal \(P\) helicene units. These inferences are further confirmed by the observed specific OR (\([\alpha]_{D}^{23}\)) value of −222° (\(c = 0.047\), CHCl\(_3\)) for \((M,M,M,P,P,P)-3\). \((M)-[7]\)Helicene\(^{21}\) has a much larger specific OR of −6200°. Despite of the
more pronounced helical twist of internal \((P)\)-[5]helicene, the much larger OR value of external \((M)\)-[7]helicene resulted in the net negative value. The assigned absolute configuration of \((M,M,M,P,P,P)\)-3 is further confirmed by the reproduced experimental ECD spectrum with TD-DFT calculations (Figure 5). Similar to OR, the negative cotton effect in the low energy region \((460 \text{ nm}, \Delta \varepsilon = -72 \text{ M}^{-1} \text{ cm}^{-1}, g = \Delta \varepsilon / \varepsilon = 3.3 \times 10^{-3})\) stems from the external \((M)\)-[7]helicene units. The anisotropic factor \(g\) is in the order of \(10^{-3}\) through the complete spectral range.

**Figure 5.** Experimental (red line, \(c = 1.4 \times 10^{-5} \text{ M}\)) and calculated (black vertical lines, TD-DFT, UB3LYP/6-31G(d,p)) ECD spectrum of \((M,M,M,P,P,P)\)-3 in chloroform.

Previously, it was observed that the solvent polarity has a large influence on the two photon cross-section value.\(^{22}\) Therefore, the two-photon absorption (TPA) cross-section of \((M,M,M,P,P,P)\)-3 was measured in two solvents with large difference in polarity, THF and toluene, via two-photon induced fluorescence relative spectroscopic technique (Figure 6). The observed overlap between one- and two-photon absorption spectra is, on one hand, attributed
to the non-centrosymmetric molecule, where the parity selection rule does not hold. On the other hand, it is caused by the high density of states, see Figure 4. The maximum non-linear absorption occurs at higher energy transitions when compared with the linear absorption maximum. This is in consistence with previously published TPA data. The maximum TPA cross-section of \((M,M,M,P,P)\)-3 is 436 GM in toluene, which increased by a factor of 1.2 to 517 GM in high polarity solvent THF. Two-photon excitation was verified by log-log plots of fluorescence intensities vs. excitation power at various wavelengths, all give slopes of 2 (Figure S3). The higher two-photon induced fluorescence signal is recorded upon excitation with CPL than the linearly polarized light (Figure S3). This indicates that the ratio of the TPA cross-section for circularly and linearly polarized excitation is greater than 1 (\(\Omega > 1\)), attributing to opposite symmetry of ground and excited states. This is in concomitance with the observed overlap of one- and two-photon absorption spectrum.

**Figure 6.** One-photon absorption spectra (blue lines) and two-photon absorption spectra (red lines) of \((M,M,M,P,P)\)-3 in THF (solid line) and Toluene (dotted line).
CONCLUSION

In summary, we have successfully achieved the stereospecific synthesis of a large propeller-shaped PAH, \((M,M,M,P,P,P)\)-3, in gram quantities and in an enantiomerically pure form, benefiting from the configurational stability of [7]helicene units and flexibility of [5]helicene units at elevated temperatures. The exclusive formation of \((M,M,M,P,P,P)\)-3 out of the four possible diastereomers is rationalized by the thermodynamic control of the reaction and kinetic flexibility of [5]helicene units under the given reaction conditions. The highly twisted structure of \((M,M,M,P,P,P)\)-3 offers unique photophysical and non-linear optical properties. Our findings provide an insight how the OR values are changed in propeller shaped PAHs with multiple helicene subunits, this will guide in designing the molecules with larger OR. We believe that access to optically active compounds, such as 3, in large quantities will push their applications in organic electronic devices.

ASSOCIATED CONTENT

Supporting Information

Supporting information (PDF)
Crystallographic data for 3 (CIF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Stereospecific synthesis and photophysical properties of propeller-shaped C\textsubscript{90}H\textsubscript{48} PAH

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S1. Synthesis

Materials.

All chemicals and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. The reactions and experiments that are sensitive to dioxygen were performed using Schlenk techniques and nitrogen-saturated solvents. The NMR experiments were performed on NMR spectrometers operating at 400 or 600 MHz proton frequencies. Standard pulse sequences were used and the data was processed using 2-fold zero-filling in the indirect dimension for all 2D experiments. Chemical shifts (δ) are reported in parts per million (ppm) relative to the solvent residual peak (¹H and ¹³C NMR, respectively): CDCl₃ (δ = 7.26 and 77.16 ppm).

Synthesis of (M,M,M,P,P,P)-3.

The 10 ml microwave reaction tube was charged with M-9,10-dibromo[7]helicene (200.0 mg, 0.37 mmol), Ni(COD)₂ (150 mg, 0.54 mmol), 2,2’-bipyridine (112 mg, 0.78 mmol), cis-1,5-cyclooctadiene (0.26 mL, 2.12 mmol) and dry THF (5 mL) under nitrogen atmosphere. The reaction tube was heated under microwave irradiation for 30 min at 110°C (internal temperature of tube). The solvent was evaporated and the residue was purified by column chromatography over silica gel using petroleum ether:Toluene (1:1) as an eluent to afford the desired product (80 mg, 57%) as an orange crystalline solid. m.p. > 300 °C; [α]²³ᵇ = −222 (c = 0.047, CHCl₃); UV/Vis (chloroform): λₘₐₓ = 418 nm (ε = 77,276 M⁻¹ cm⁻¹); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.95(d, J = 8.6 Hz, 1H), 8.04(d, J = 8.6 Hz, 1H), 7.78(d, J = 8.5Hz,1H), 7.61(d, J = 8.5 Hz, 1H), 7.59(d, J = 8.4 Hz, 1H), 7.44(d, J = 7.6 Hz, 1H), 7.09(t, J = 7.9 Hz, 1H), 6.73(t, J = 8.3 Hz,1H); ¹³C NMR (101 MHz, CDCl₃, δ ppm): 132.68, 131.90, 131.47, 129.97, 129.27, 128.86, 128.14, 127.81, 127.38, 126.35, 125.74, 125.52, 124.87, 124.02; HRMS (MALDI-TOF) m/z: Calcd for C₉₀H₄₈: 1128.3756; Found: 128.3719.
S2. UV–vis spectroscopy

Figure 1. UV–vis spectra of \((M,M,M,P,P,P)-3\) in toluene, chloroform and THF. Inset: magnified image of low energy absorption.
S3. Theoretical Calculations

All DFT calculations were performed in Gaussian 16 suite of electronic structure programs. Geometries were optimized using B3LYP functional and 6-31G(d,p) basis set in the gas phase. SpecDis and Avogadro softwares were used to analyze the TD-DFT calculated spectra and to generate graphical images of frontier molecular orbitals (FMOs), respectively.

Figure 2. Optimized structure of (M,M,M,P,P,P)-3.

[1]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16 Rev. C.01, Wallingford, CT, 2016.
Table S1. Frontier molecular orbitals and energies.

| Energy (eV) | Orbitals |
|-------------|----------|
| LUMO+1      | −1.928   |
| LUMO        | −1.928   |
| HOMO        | −5.064   |
| HOMO−1      | −5.064   |
Table S2. NICS calculation.

The nucleus independent chemical shift (NICS) calculations were performed on B3LYP/6-31G(d,p) optimized geometries at the GIAO-B3LYP/6-31G(d,p) level. Considering the non-planarity of the molecules, NICS(1) values were obtained by placing dummy atoms 1 Å above (purple) and below (green) each benzenoid ring. NICS(0) values were obtained by placing dummy atoms in the center of the ring.

| Ring | NICS (1) above (purple) | NICS (1) below (green) | NICS (0) (orange) |
|------|-------------------------|------------------------|------------------|
| A    | –4.0                    | –4.0                   | –11.6            |
| B    | –16.7                   | –16.7                  | –9.1             |
| C    | –18.1                   | –18.0                  | –5.1             |
| D    | –18.4                   | –18.7                  | –6.3             |
| E    | –27.9                   | –27.1                  | –8.0             |
**Table S3. TD-DFT calculations.**

TD-DFT calculations were performed on B3LYP/6-31G(d,p) optimized geometries at the B3LYP/6-31g(d,p) level including chloroform as a solvent.

| Wavelength (nm) | Major transitions       | Contribution | oscillator strength (f) |
|-----------------|-------------------------|--------------|-------------------------|
| 473             | HOMO−1→LUMO             | 0.19         |                         |
|                 | HOMO−1→LUMO+1           | 0.45         |                         |
|                 | HOMO→LUMO               | 0.46         | 0.10                    |
| 447             | HOMO−1→LUMO             | 0.49         |                         |
|                 | HOMO→LUMO+1             | 0.49         | 1.05                    |
| 447             | HOMO−1→LUMO+1           | 0.49         |                         |
|                 | HOMO→LUMO               | 0.49         | 1.05                    |
S3. Two-photon induced fluorescence spectroscopy

The TPA measurements of the compound in THF and Toluene were performed using the two-photon fluorescence technique.

A Ti: sapphire amplifier (Solstice, Spectra Physics) operating at 1 kHz, delivering 100 fs pulses at 800 nm served as the pulse source. 70% of the available energy (2.5 mJ) seeds a tunable computer-controlled optical parametric amplifier (TOPAS-C, Light Conversion) which is used as the excitation source. The excitation energy varies in the 0.2 – 3 μJ range by using a series of three thin broadband polarizers and a mechanical rotational mount. Excitation of the samples was achieved by using a protected silver parabolic mirror. The emitted fluorescence signal was collected at 90° using an achromatic lens and then directed to a compact CCD spectrometer for detection. Coumarin 485 in Methanol was used as a secondary reference standard. Maintenance of identical excitation conditions for reference and samples was achieved using a high precision motorized rotational stage.

The two-photon excitation was verified by evaluation of the emitted signal’s quadratic dependence with respect the excitation energy for each individual measurement. The log-log plots of fluorescence intensity vs. excitation energy giving slopes of 2. By introducing an achromatic quarter-wave plate into the excitation laser beam, we recorded the fluorescence signal by using right- and left-handed circular polarized excitation light (see Figure 3).

The TPA Polarization ratio (Ω(TPA)) defined as: 

\[ \Omega_{\text{TPA}} = \frac{\sigma_{\text{circular, TPA}}}{\sigma_{\text{linear, TPA}}} \]

where \( \sigma_{\text{circular, TPA}} \) and \( \sigma_{\text{linear, TPA}} \) are the TPA cross-section for circularly and linearly polarized excitation light respectively.
Figure 3. Power dependence of the emission intensity of \((M,M,M,P,P,P)-3\) in THF at selected excitation wavelength under linear polarized (red squares), right-handed circular polarized (blue circles) and left-handed circular polarized (green circles) excitation laser beam.
Figure 4. MALDI-TOF mass of (M,M,M,P,P,P)-3.
S6. NMR spectroscopy

Figure S5. Assignment of $^1$H (blue) and $^{13}$C NMR (black) peaks for (M,M,M,P,P,P)-3. Note two carbon peaks (red) are assigned tentatively.
Figure S6. $^1$H and $^{13}$C NMR spectra for (M,M,M,P,P,P)-3.
Figure S7. COSY and NOESY for \((M,M,P,P,P)\)-3.
Figure S8. HSQC and HMBC for (M,M,M,P,P,P)-3.
S7. Crystallographic data

A crystal was mounted onto a sample loop with least required exposure out of the mother liquor and immediately cooled to 100 K under continuous nitrogen flow. Crystal data were collected on a Bruker D8Quest Kappa Diffractometer using Cu Kα radiation ($\lambda = 1.54178$ Å) from an Incoatec IµS micro-source with Montel multilayered mirror, a Photon II CPAD area detector and Apex3* software.

The structure was solved using direct methods, refined with the SHELXL software package1 and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions.

The residual electron density could not be assigned to the solvent molecule. Therefore, the SQUEEZE routine of PLATON was used to remove the electron density.

Details about the Squeezed Material loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
    1 -0.061  0.250  0.500   971   228 ''
    2  0.034  0.750  1.000   972   228 ''
  _platon_squeeze_void_probe_radius      1.20
  _platon_squeeze_details

The remaining structure could be refined nicely.

$wR^2 = 0.0900$, $GooF = S = 1.027$, Restrainted $GooF = 1.027$ for all data
$R1 = 0.0331$ for 13210 $F_o > 4\sigma(F_o)$ and 0.0360 for all 14027 data

Flack $x = 0.705(511)$ by classical fit to all intensities
0.499(158) from 5733 selected quotients (Parsons' method)

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1956871. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif.

[1] G. M. Sheldrick, Acta Crystallogr. A 2008, 64, 112-122.
### Table S4. Crystallographic table.

| Compound | (M,M,M,P,P,P)-3 |
|----------|-----------------|
| CCDC number | 1956871 |
| Chemical formula | C_{90}H_{48} |
| $M_r$ | 1129.28 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 15.6063(10), 17.4064(12), 26.0905(16) |
| $\alpha$, $\beta$, $\gamma$ (°) | 90, 90, 90 |
| $V$ (Å$^3$) | 7087.5 (8) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.46 |
| Crystal size (mm) | 0.28 × 0.16 × 0.14 |
| $T_{\text{min}}, T_{\text{max}}$ | 0.556, 0.754 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 118614, 14027, 13210 |
| $R_{\text{int}}$ | 0.047 |
| (sin $\theta$/$\lambda$)$_{\text{max}}$ (Å$^{-1}$) | 0.619 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.033, 0.090, 1.03 |
| No. of reflections | 14027 |
| No. of parameters | 812 |
| Absolute structure parameter | 0.50 (16) |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å$^{-3}$) | 0.14, −0.12 |
Figure S9. Structure and packing of (M,M,M,P,P)-3.
S8. Cartesian Coordinates

\((M,M,M,P,P,P)\)-3, (B3LYP/6-31G(d,p), gas phase), \(E = -3458.69365941\) Hartree

|   |          |          |          |          |
|---|-----------|-----------|-----------|-----------|
|   | C         |          |          |          |
|   | 1.40560   | 0.19400  | -0.06590 |          |
|   | -3.19770  | 1.92410  | -0.47390 |          |
|   | -3.62440  | 0.88840  | 0.47380  |          |
|   | -1.79900  | 2.14810  | -0.54520 |          |
|   | -2.78970  | -0.25610 | 0.54510  |          |
|   | -0.87060  | 1.12070  | -0.06440 |          |
|   | -1.31810  | 3.27350  | -1.27130 |          |
|   | -4.08530  | 2.67930  | -1.32560 |          |
|   | -3.57850  | 3.87050  | -1.91720 |          |
|   | -2.18870  | 4.14690  | -1.86310 |          |
|   | -4.45440  | 4.78120  | -2.58980 |          |
|   | -5.77730  | 4.50480  | -2.73570 |          |
|   | -6.29970  | 3.23590  | -2.33040 |          |
|   | -5.45090  | 2.28950  | -1.67300 |          |
|   | -7.63330  | 2.88700  | -2.65120 |          |
|   | -8.11930  | 1.62070  | -2.40360 |          |
|   | -7.26150  | 0.65350  | -1.84840 |          |
|   | -5.96580  | 0.98100  | -1.49620 |          |
|   | -4.78600  | 0.97800  | 1.32590  |          |
|   | -5.26590  | -0.22430 | 1.91760  |          |
|   | -4.47440  | -1.39970 | 1.86350  |          |
|   | -3.24130  | -1.39350 | 1.27140  |          |
|   | -5.48030  | 2.21690  | 1.67320  |          |
|   | -6.74950  | 2.14360  | 2.33050  |          |
|   | -7.27300  | 0.87510  | 2.73570  |          |
|   | -6.52920  | -0.25320 | 2.59000  |          |
|   | -7.44970  | 3.33080  | 2.65190  |          |
|   | -6.90210  | 4.57180  | 2.40460  |          |
|   | -5.61210  | 4.65360  | 1.84900  |          |
|   | -4.92370  | 3.50830  | 1.49620  |          |
|   | -1.40730  | -0.18140 | 0.06350  |          |
|   | -0.06770  | -3.73090 | -0.47450 |          |
|   | 1.04300   | -3.58250 | 0.47270  |          |
|   | -0.96090  | -2.63150 | -0.54600 |          |
|   | 1.61720   | -2.28750 | 0.54300  |          |
|   | -2.17610  | -2.77770 | -1.27190 |          |
|   | -0.27820  | -4.87730 | -1.32590 |          |
|   | -1.56340  | -5.03420 | -1.91710 |          |
|   | -2.49750  | -3.96860 | -1.86320 |          |
|   | -1.91440  | -6.24840 | -2.58890 |          |
|   | -1.01360  | -7.25590 | -2.73460 |          |
|   | 0.34680   | -7.07360 | -2.33040 |          |
|   | 0.74210   | -5.86510 | -1.67350 |          |
|   | 1.31590   | -8.05360 | -2.65210 |          |
|   | 2.65570   | -7.84090 | -2.40540 |          |
|   | 3.06440   | -6.61440 | -1.85030 |          |
|   | X   | Y     | Z     |
|---|-----|-------|-------|
| C | 2.1327 | -5.6564 | -1.4973 |
| C | 1.5465 | -4.6333 | 1.3247 |
| C | 2.8283 | -4.4481 | 1.9150 |
| C | 3.4510 | -3.1753 | 1.8594 |
| C | 2.8290 | -2.1104 | 1.2679 |
| C | 0.8201 | -5.8532 | 1.6737 |
| C | 1.5177 | -6.9152 | 2.3321 |
| C | 2.8786 | -6.7351 | 2.7356 |
| C | 3.4848 | -5.5275 | 2.5878 |
| C | 0.8385 | -8.1139 | 2.6560 |
| C | -0.5103 | -8.2593 | 2.4096 |
| C | -1.2253 | -7.1835 | 1.8520 |
| C | -0.5767 | -6.0159 | 1.4970 |
| C | 3.2647 | 1.8076 | 0.4755 |
| C | 2.5818 | 2.6943 | 0.4733 |
| C | 2.7590 | 0.4846 | -0.5478 |
| C | 1.1733 | 2.5443 | 0.5446 |
| C | 3.4923 | -0.4941 | -1.2757 |
| C | 4.3623 | 2.1992 | -1.3273 |
| C | 5.1399 | 1.1651 | -1.9204 |
| C | 4.6837 | -0.1765 | -1.8678 |
| C | 6.3666 | 1.4686 | -2.5927 |
| C | 6.7893 | 2.7524 | -2.7371 |
| C | 5.9520 | 3.8392 | -2.3306 |
| C | 4.7081 | 3.5770 | -1.6732 |
| C | 6.3170 | 5.1688 | -2.6502 |
| C | 5.4638 | 6.2292 | -2.4011 |
| C | 4.1976 | 5.9635 | -1.8455 |
| C | 3.8329 | 4.6774 | -1.4944 |
| C | 3.2410 | 3.6541 | 1.3263 |
| C | 2.4403 | 4.6708 | 1.9189 |
| C | 1.0266 | 4.5744 | 1.8640 |
| C | 0.4147 | 3.5044 | 1.2710 |
| C | 4.6609 | 3.6341 | 1.6743 |
| C | 5.2327 | 4.7682 | 2.3338 |
| C | 4.3968 | 5.8560 | 2.7403 |
| C | 3.0477 | 5.7778 | 2.5933 |
| C | 6.6109 | 4.7793 | 2.6553 |
| C | 6.8360 | 2.5278 | 1.8480 |
| C | 5.4999 | 2.5060 | 1.4954 |
| C | 0.5463 | 1.3098 | 0.0631 |
| C | 0.8610 | -1.1275 | 0.0622 |
| C | -0.5352 | -1.3138 | -0.0651 |
| C | 7.4110 | 3.6844 | 2.4058 |
| H | -0.2524 | 3.4368 | -1.3577 |
| H | -1.8140 | 5.0319 | -2.3700 |
| H | -4.0336 | 5.7069 | -2.9731 |
| H | -6.4443 | 5.2114 | -3.2220 |
| H | -8.2619 | 3.6348 | -3.1278 |
| H | -9.1417 | 1.3625 | -2.6633 |
| H   | -7.61340 | -0.36330 | -1.70190 |
|-----|----------|----------|----------|
| H   | -5.32630 | 0.20550  | -1.09970 |
| H   | -4.83220 | -2.29160 | 2.37060  |
| H   | -2.60030 | -2.26030 | 1.35800  |
| H   | -8.24420 | 0.84370  | 3.22200  |
| H   | -6.88290 | -1.20650 | 2.97340  |
| H   | -8.42250 | 3.24320  | 3.12860  |
| H   | -7.44540 | 5.47540  | 2.66480  |
| H   | -5.14520 | 5.62320  | 1.70250  |
| H   | -3.92380 | 3.60780  | 1.09890  |
| H   | -2.85030 | -1.93650 | -1.35870 |
| H   | -3.45130 | -4.08670 | -2.37000 |
| H   | -2.92660 | -6.34720 | -2.97170 |
| H   | -1.29230 | -8.18700 | -3.22050 |
| H   | 0.98260  | -8.97200 | -3.12850 |
| H   | 3.39050  | -8.59690 | -2.66570 |
| H   | 4.12100  | -6.41040 | -1.70440 |
| H   | 2.48430  | -4.71480 | -1.10090 |
| H   | 4.40290  | -3.03930 | 2.36550  |
| H   | 3.25980  | -1.12200 | 1.35400  |
| H   | 3.39110  | -7.56040 | 3.22240  |
| H   | 4.48780  | -5.35780 | 2.96980  |
| H   | 1.40030  | -8.91230 | 3.13400  |
| H   | -1.02190 | -9.18060 | 2.67170  |
| H   | -2.29850 | -7.26340 | 1.70580  |
| H   | -1.16200 | -5.19980 | 1.09840  |
| H   | 3.10040  | -1.49830 | -1.36330 |
| H   | 5.26230  | -0.94300 | -2.37610 |
| H   | 6.95760  | 0.64160  | -2.97690 |
| H   | 7.73480  | 2.97690  | -3.22330 |
| H   | 7.27870  | 5.33940  | -3.12690 |
| H   | 5.75170  | 7.23750  | -2.65980 |
| H   | 3.49340  | 6.77690  | -1.69750 |
| H   | 2.84210  | 4.51130  | -1.09690 |
| H   | 0.43350  | 5.33030  | 2.37150  |
| H   | -0.65670 | 3.38360  | 1.35720  |
| H   | 4.85570  | 6.71160  | 3.22810  |
| H   | 2.39960  | 6.56100  | 2.97720  |
| H   | 7.02210  | 5.66440  | 3.13370  |
| H   | 7.44160  | 1.63860  | 1.69980  |
| H   | 5.08530  | 1.59140  | 1.09650  |
| H   | 8.46520  | 3.70190  | 2.66590  |
\((M,M,M,M,M)\)-3, (B3LYP/6-31G(d,p), gas phase), \(E = -3458.66405545\) Hartree

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C | -1.29340 | 0.62650 | 0.06620 |   |   |
| C | 3.62020  | 0.86420 | -0.43300 |   |   |
| C | 3.70950  | -0.30230 | 0.43520 |   |   |
| C | 2.33560  | 1.23470 | -0.92040 |   |   |
| C | 2.49640  | -0.86280 | 0.92440 |   |   |
| C | 1.12370  | 0.71710 | -0.31420 |   |   |
| C | 2.24610  | 1.99430 | -2.12790 |   |   |
| C | 4.72550  | 1.73080 | -0.82710 |   |   |
| C | 4.62330  | 2.40950 | -2.07000 |   |   |
| C | 3.37130  | 2.45570 | -2.74780 |   |   |
| C | 5.76090  | 3.07910 | -2.62130 |   |   |
| C | 6.92690  | 3.17710 | -1.92440 |   |   |
| C | 6.99800  | 2.71700 | -0.57320 |   |   |
| C | 5.88270  | 2.02990 | 0.00190  |   |   |
| C | 8.13180  | 3.00790 | 0.22430  |   |   |
| C | 8.15430  | 2.70340 | 1.56840  |   |   |
| C | 7.02000  | 2.11580 | 2.16290  |   |   |
| C | 5.91700  | 1.79010 | 1.39910  |   |   |
| C | 4.93360  | -0.99160 | 0.82820  |   |   |
| C | 4.93690  | -1.67630 | 2.07210  |   |   |
| C | 3.70720  | -1.90990 | 2.75210  |   |   |
| C | 2.52430  | -1.62510 | 2.13320  |   |   |
| C | 6.12110  | -1.11370 | -0.00260 |   |   |
| C | 7.32810  | -1.62500 | 0.57080  |   |   |
| C | 7.32940  | -2.08880 | 1.92260  |   |   |
| C | 6.16330  | -2.16630 | 2.62180  |   |   |
| C | 8.49110  | -1.74310 | -0.22880 |   |   |
| C | 8.46530  | -1.43980 | -1.57310 |   |   |
| C | 7.25460  | -1.02930 | -2.16570 |   |   |
| C | 6.11660  | -0.87220 | -1.40000 |   |   |
| C | 1.21960  | -0.53620 | 0.31830  |   |   |
| C | -1.09920 | -3.61840 | 0.22330  |   |   |
| C | -2.15530 | -3.04130 | -0.59440 |   |   |
| C | 0.10950  | -2.86960 | 0.32440  |   |   |
| C | -2.24210 | -1.62450 | -0.63340 |   |   |
| C | 1.31400  | -3.63040 | 0.45000  |   |   |
| C | -1.15990 | -4.92120 | 0.85550  |   |   |
| C | 0.06080  | -5.61280 | 1.06460  |   |   |
| C | 1.28540  | -4.96510 | 0.74340  |   |   |
| C | 0.06200  | -6.95670 | 1.55020  |   |   |
| C | -1.10050 | -7.58570 | 1.87590  |   |   |
| C | -2.34560 | -6.88590 | 1.82020  |   |   |
| C | -2.38670 | -5.53760 | 1.34110  |   |   |
| C | -3.53000 | -7.50330 | 2.29100  |   |   |
| C | -4.72180 | -6.81340 | 2.34450  |   |   |
| C | -4.75450 | -5.46280 | 1.94630  |   |   |
| C | -3.61810 | -4.84480 | 1.46280  |   |   |
| C | -3.05590 | -3.82290 | -1.42430 |   |   |
|   |         |         |         |
|---|---------|---------|---------|
| C|-4.24050 | -3.19380| -1.88920|
| C|-4.35560 | -1.77830| -1.82030|
| C|-3.34600 | -1.01810| -1.30650|
| C|-2.80320 | -5.17960| -1.89880|
| C|-3.88040 | -5.93060| -2.46820|
| C|-5.14550 | -5.30230| -2.68990|
| C|-5.28990 | -3.96550| -2.48120|
| C|-3.66160 | -7.26020| -2.90330|
| C|-2.40350 | -7.82250| -2.86940|
| C|-1.31540 | -7.04670| -2.42560|
| C|-1.51210 | -5.76280| -1.95510|
| C|-2.59650 | 2.67690 | 0.59170 |
| C|-1.63740 | 3.41000 | 0.22070 |
| C|-2.46640 | 1.26340 | 0.62910 |
| C|-0.32860 | 2.85390 | 0.31890 |
| C|-3.46750 | 0.49470 | 1.29710 |
| C|-3.60930 | 3.31060 | 1.41840 |
| C|-4.68630 | 2.50750 | 1.87700 |
| C|-4.58360 | 1.09120 | 1.80680 |
| C|-5.84410 | 3.10920 | 2.46400 |
| C|-5.90650 | 4.45210 | 2.67410 |
| C|-4.75080 | 5.26630 | 2.45960 |
| C|-3.56870 | 4.68900 | 1.89560 |
| C|-4.73940 | 6.61300 | 2.89690 |
| C|-3.58140 | 7.36030 | 2.87060 |
| C|-2.38540 | 6.75990 | 2.43260 |
| C|-2.38180 | 5.46190 | 1.95980 |
| C|-1.89310 | 4.69030 | 0.85000 |
| C|-0.79090 | 5.56010 | 1.05240 |
| C| 0.51680 | 5.10470 | 0.72870 |
| C| 0.74690 | 3.78900 | 0.43880 |
| C|-3.19750 | 5.11490 | 1.33870 |
| C|-3.36030 | 6.45560 | 1.81280 |
| C|-2.23590 | 7.33680 | 1.86120 |
| C|-0.99240 | 6.89040 | 1.53360 |
| C|-4.62310 | 6.88760 | 2.28650 |
| C|-5.69580 | 6.02450 | 2.34790 |
| C|-5.52390 | 4.68300 | 1.95490 |
| C|-4.30860 | 4.24320 | 1.46850 |
| C|-0.15840 | 1.40720 | 0.23570 |
| C|-1.18220 | -0.81590| -0.06690|
| C| 0.05790 | -1.41390| 0.23870|
| H| 1.27000 | 2.13820 | -2.57640|
| H| 3.31180 | 2.94110 | -3.71760|
| H| 5.66740 | 3.51640 | -3.61170|
| H| 7.79250 | 3.67350 | -2.35430|
| H| 8.97690 | 3.50810 | -0.24160|
| H| 9.02480 | 2.94340 | 2.17170 |
| H| 7.00570 | 1.92570 | 3.23190 |
| H| 5.04850 | 1.36670 | 1.88530 |
|   |   |   |   |
|---|---|---|---|
| H | 3.72300 | -2.39700 | 3.72270 |
| H | 1.58180 | -1.91440 | 2.58320 |
| H | 8.26070 | -2.44900 | 2.35120 |
| H | 6.13860 | -2.61140 | 3.61280 |
| H | 9.40260 | -2.11030 | 0.23580 |
| H | 9.36080 | -1.54690 | -2.17800 |
| H | 7.21000 | -0.84420 | -3.23480 |
| H | 5.19350 | -0.58420 | -1.88460 |
| H | 2.26550 | -3.15160 | 0.27750 |
| H | 2.21110 | -5.53120 | 0.79390 |
| H | 1.01610 | -7.46750 | 1.64770 |
| H | -1.09650 | -8.61330 | 2.22910 |
| H | -3.47430 | -8.53380 | 2.63210 |
| H | -5.62140 | -7.29660 | 2.71420 |
| H | -5.67750 | -4.89650 | 2.02830 |
| H | -3.66970 | -3.80020 | 1.18830 |
| H | -5.22830 | -1.30580 | -2.26270 |
| H | -3.39190 | 0.05920 | -1.38460 |
| H | -5.95620 | -5.89270 | -3.10820 |
| H | -6.21020 | -3.45530 | -2.75240 |
| H | -4.50440 | -7.81830 | -3.30290 |
| H | -2.24490 | -8.83830 | -3.21910 |
| H | -0.30910 | -7.45290 | -2.46300 |
| H | -0.65110 | -5.17950 | -1.65970 |
| H | -3.34870 | -0.57700 | 1.37450 |
| H | -5.37590 | 0.49030 | 2.24490 |
| H | -6.67720 | 2.46420 | 2.73030 |
| H | -6.79990 | 4.91150 | 3.08830 |
| H | -5.65950 | 7.03560 | 3.29210 |
| H | -3.58130 | 8.38780 | 3.22190 |
| H | -1.45290 | 7.31450 | 2.47610 |
| H | -1.44040 | 5.01690 | 1.66890 |
| H | 1.34600 | 5.80500 | -0.77440 |
| H | 1.75950 | 3.45950 | -0.26450 |
| H | -2.38710 | 8.35450 | -2.21080 |
| H | -0.12660 | 7.54060 | -1.62600 |
| H | -4.72370 | 7.91610 | -2.62360 |
| H | -6.65700 | 6.36670 | -2.71980 |
| H | -6.34950 | 3.98300 | -2.04320 |
| H | -4.20160 | 3.20160 | -1.19830 |
(M,M,M,M,P)-3, (B3LYP/6-31G(d,p), gas phase), $E = -3458.66921549$ Hartree

| C    | -1.24760 | -0.60890 | 0.34860 |
|------|----------|----------|---------|
| C    | 1.14270  | 3.59890  | 0.01300 |
| C    | 2.40490  | 2.87830  | -0.00890|
| C    | -0.06040 | 2.86850  | -0.21830|
| C    | 2.35750  | 1.49840  | 0.31990 |
| C    | -0.03280 | 1.40800  | -0.28530|
| C    | -1.28080 | 3.60340  | -0.31110|
| C    | 1.04990  | 5.00640  | 0.37120 |
| C    | -0.12820 | 5.70800  | 0.01150 |
| C    | -1.29140 | 4.96880  | -0.32460|
| C    | -0.17210 | 7.13770  | 0.06610 |
| C    | 0.87600  | 7.85070  | 0.55990 |
| C    | 1.96850  | 7.17410  | 1.18860 |
| C    | 2.02870  | 5.74460  | 1.16310 |
| C    | 2.92810  | 7.90750  | 1.92770 |
| C    | 3.87110  | 7.26680  | 2.70270 |
| C    | 3.85480  | 5.86110  | 2.78400 |
| C    | 2.95850  | 5.12380  | 2.03470 |
| C    | 3.71010  | 3.46490  | -0.25410|
| C    | 4.83100  | 2.86450  | 0.37550 |
| C    | 4.65590  | 1.65320  | 1.10540 |
| C    | 3.48800  | 0.95250  | 1.00680 |
| C    | 3.94710  | 4.58510  | -1.15070|
| C    | 5.25150  | 5.17140  | -1.20340|
| C    | 6.31370  | 4.61490  | -0.42610|
| C    | 6.11820  | 3.48020  | 0.30120 |
| C    | 5.49680  | 6.26540  | -2.06900|
| C    | 4.51240  | 6.74950  | -2.90330|
| C    | 3.24740  | 6.12910  | -2.91110|
| C    | 2.97620  | 5.07560  | -2.06090|
| C    | 1.16860  | 0.72730  | 0.01650 |
| C    | 2.39140  | -2.88940 | 0.00970 |
| C    | 1.12580  | -3.60400 | -0.01220|
| C    | 2.35050  | -1.50920 | -0.31860|
| C    | -0.07380 | -2.86810 | 0.21950 |
| C    | 3.48340  | -0.96840 | -1.00550|
| C    | 3.69390  | -3.48220 | 0.25460 |
| C    | 4.81750  | -2.88690 | -0.37490|
| C    | 4.64790  | -1.67460 | -1.10450|
| C    | 6.10180  | -3.50860 | -0.30090|
| C    | 6.29200  | -4.64450 | 0.42610 |
| C    | 5.22730  | -5.19620 | 1.20340 |
| C    | 3.92570  | -4.60370 | 1.15100 |
| C    | 5.46760  | -6.29160 | 2.06860 |
| C    | 4.48110  | -6.77130 | 2.90280 |
| C    | 3.21910  | -6.14480 | 2.91110 |
| C    | 2.95270  | -5.08980 | 2.06130 |
| C    | 1.02640  | -5.01080 | -0.37120|
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| H | 5.49040 | 1.25410 | 1.67460 |   |   |   |
| H | 3.39560 | -0.01750 | 1.47830 |   |   |   |
| H | 7.29180 | 5.08660 | -0.46770 |   |   |   |
| H | 6.94030 | 3.01990 | 0.84270 |   |   |   |
| H | 6.49110 | 6.70460 | -2.07750 |   |   |   |
| H | 4.71580 | 7.58420 | -3.56750 |   |   |   |
| H | 2.48000 | 6.47360 | -3.59800 |   |   |   |
| H | 2.00450 | 4.60240 | -2.10700 |   |   |   |
| H | 3.39560 | 0.00210 | -1.47680 |   |   |   |
| H | 5.48340 | -1.27930 | -1.67370 |   |   |   |
| H | 6.92600 | -3.05200 | -0.84220 |   |   |   |
| H | 7.26790 | -5.12070 | 0.46750 |   |   |   |
| H | 6.45980 | -6.73540 | 2.07670 |   |   |   |
| H | 4.68060 | -7.60720 | 3.56670 |   |   |   |
| H | 2.45020 | -6.48590 | 3.59810 |   |   |   |
| H | 1.98330 | -4.61200 | 2.10780 |   |   |   |
| H | -2.24570 | -5.49590 | 0.49650 |   |   |   |
| H | -2.23140 | -3.07000 | 0.40940 |   |   |   |
| H | 0.81480 | -8.94040 | -0.57480 |   |   |   |
| H | -1.10000 | -7.63230 | 0.30010 |   |   |   |
| H | 2.83670 | -9.00500 | -1.90690 |   |   |   |
| H | 4.55490 | -7.85900 | -3.28040 |   |   |   |
| H | 4.51780 | -5.36740 | -3.44970 |   |   |   |
| H | 2.92490 | -4.06060 | -2.14790 |   |   |   |
| H | -1.48340 | -2.04540 | 2.61330 |   |   |   |
| H | -3.49800 | -2.28430 | 4.01550 |   |   |   |
| H | -5.78390 | -1.80100 | 4.49490 |   |   |   |
| H | -7.85170 | -0.50780 | 4.08680 |   |   |   |
| H | -8.99060 | 1.28860 | 2.96160 |   |   |   |
| H | -9.01580 | 3.16280 | 1.33700 |   |   |   |
| H | -6.99330 | 3.58650 | -0.06630 |   |   |   |
| H | -5.06960 | 2.10410 | 0.05620 |   |   |   |
| H | -3.48660 | 2.30090 | -4.01460 |   |   |   |
| H | -1.47350 | 2.05290 | -2.61170 |   |   |   |
| H | -7.84790 | 0.54320 | -4.08780 |   |   |   |
| H | -5.77440 | 1.82750 | -4.49500 |   |   |   |
| H | -8.99500 | -1.24820 | -2.96310 |   |   |   |
| H | -9.02920 | -3.12230 | -1.33850 |   |   |   |
| H | -7.00920 | -3.55480 | 0.06570 |   |   |   |
| H | -5.07880 | -2.08080 | -0.05610 |   |   |   |
(M,M,M,M,M,M)-3, (B3LYP/6-31G(d,p), gas phase), E = −3458.65698647 Hartree

|   |      |      |      |
|---|------|------|------|
| C | -0.74130 | -1.21510 | -0.06190 |
| C | -0.66190 | 3.75460 | -0.10910 |
| C | 0.77640 | 3.73260 | 0.10850 |
| C | -1.31560 | 2.52240 | -0.38150 |
| C | 1.39190 | 2.48090 | 0.38080 |
| C | -0.68180 | 1.24930 | -0.06240 |
| C | -2.53830 | 2.56090 | -1.12450 |
| C | -1.50380 | 4.94340 | -0.04980 |
| C | -2.69040 | 4.95370 | -0.82670 |
| C | -3.13950 | 3.74670 | -1.43310 |
| C | -3.43910 | 6.16160 | -0.98730 |
| C | -3.08940 | 7.29890 | -0.32520 |
| C | -2.03510 | 7.27580 | 0.63960 |
| C | -1.26250 | 6.08500 | 0.81910 |
| C | -1.80300 | 8.39740 | 1.47300 |
| C | -0.88990 | 8.34220 | 2.50390 |
| C | -0.19630 | 7.14030 | 2.74830 |
| C | -0.38080 | 6.04440 | 1.92920 |
| C | 1.65420 | 4.89520 | 0.04960 |
| C | 2.84070 | 4.86880 | 0.82630 |
| C | 3.25270 | 3.64850 | 1.43220 |
| C | 2.61530 | 2.48170 | 1.12350 |
| C | 1.44770 | 6.04410 | -0.81850 |
| C | 2.25640 | 7.21070 | -0.63860 |
| C | 3.31120 | 7.20090 | 0.32580 |
| C | 3.62610 | 6.05300 | 0.98720 |
| C | 2.05830 | 8.33940 | -1.47100 |
| C | 1.14340 | 8.31310 | -2.50140 |
| C | 0.41320 | 7.13310 | -2.74640 |
| C | 0.56460 | 6.03140 | -1.92830 |
| C | 0.71930 | 1.22790 | 0.06180 |
| C | 3.58260 | -1.30390 | -0.10900 |
| C | 2.84450 | -2.53860 | 0.10890 |
| C | 2.84210 | -0.12190 | -0.38150 |
| C | 1.45280 | -2.44600 | 0.38140 |
| C | 3.48650 | 0.91770 | -1.12450 |
| C | 5.03310 | -1.16910 | -0.05000 |
| C | 5.63510 | -0.14650 | -0.82700 |
| C | 4.81410 | 0.84570 | -1.43320 |
| C | 7.05530 | -0.10180 | -0.98780 |
| C | 7.86570 | -0.97340 | -0.32610 |
| C | 7.31900 | -1.87520 | 0.63850 |
| C | 5.90150 | -1.94890 | 0.81850 |
| C | 8.17460 | -2.63740 | 1.47120 |
| C | 7.67070 | -3.40120 | 2.50180 |
| C | 6.28310 | -3.40100 | 2.74690 |
| C | 5.42600 | -2.69270 | 1.92860 |
| C | 3.41260 | -3.87990 | 0.04990 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 2.79690   | -4.89440  | 0.82700   |
| C       | 1.53430   | -4.64100  | 1.43330   |
| C       | 0.84230   | -3.50580  | 1.12460   |
| C       | 4.51040   | -4.27550  | -0.81880  |
| C       | 5.11660   | -5.55900  | 0.82700   |
| C       | 4.58140   | -6.46760  | 0.32580   |
| C       | 3.43010   | -6.16650  | 0.98770   |
| C       | 6.19270   | -5.95180  | -1.47210  |
| C       | 6.62640   | -5.14640  | 0.32580   |
| C       | 5.96930   | -3.92430  | 0.82700   |
| C       | 4.94000   | -3.50450  | 0.82700   |
| C       | -2.92070  | -2.45080  | 0.82700   |
| C       | -3.62090  | -1.19420  | 0.10850   |
| C       | -1.52670  | -2.40080  | 0.38060   |
| C       | -2.84490  | -0.03510  | 0.38070   |
| C       | -0.94850  | -3.47920  | -1.12290  |
| C       | -3.52930  | -3.77430  | -0.04880  |
| C       | -2.94460  | -4.80750  | -0.82500  |
| C       | -1.67460  | -4.59310  | -1.43110  |
| C       | -3.61610  | -6.05980  | -0.98530  |
| C       | -4.77630  | -6.32540  | -0.32350  |
| C       | -5.28380  | -5.40040  | 0.64060   |
| C       | -4.63890  | -4.13580  | 0.81980   |
| C       | -6.37170  | -5.75970  | 1.47350   |
| C       | -6.78120  | -4.94080  | 2.50370   |
| C       | -6.08720  | -3.73900  | 2.74790   |
| C       | -5.04530  | -3.35130  | 1.92930   |
| C       | -5.06660  | -1.01540  | 0.04890   |
| C       | -5.63750  | 0.02540   | 0.82520   |
| C       | -4.78690  | 0.99250   | 1.43140   |
| C       | -3.45770  | 1.02400   | 1.12310   |
| C       | -5.95790  | -1.76860  | -0.81990  |
| C       | -7.37260  | -1.65150  | -0.64070  |
| C       | -7.89210  | -0.73330  | 0.32350   |
| C       | -7.05580  | 0.11340   | 0.98540   |
| C       | -8.25060  | -2.38730  | -1.47390  |
| C       | -6.38260  | -3.20850  | -2.74830  |
| C       | -5.50460  | -2.52680  | -1.92950  |
| C       | -1.42330  | 0.00890   | 0.06190   |
| C       | 0.70370   | -1.23710  | 0.06220   |
| C       | 1.42270   | -0.03450  | -0.06230  |
| C       | -7.76970  | -3.16620  | -2.50420  |
| H       | -2.94690  | 1.63430   | -1.50590  |
| H       | -4.01290  | 3.77110   | -2.07830  |
| H       | -4.29920  | 6.14710   | -1.65120  |
| H       | -3.65050  | 8.21900   | -0.46410  |
| H       | -2.38560  | 9.29860   | 1.30060   |
| H       | -0.72940  | 9.20530   | 3.14310   |
| H       | 0.48150   | 7.06830   | 3.59370   |
| H       | 0.14100   | 5.12500   | 2.15850   |
| H         | 4.12650 | 3.64580 | 2.07730 |
|-----------|---------|---------|---------|
| H         | 2.99520 | 1.54300 | 1.50480 |
| H         | 3.90030 | 8.10330 | 0.46500 |
| H         | 4.48560 | 6.01190 | 1.65090 |
| H         | 2.66830 | 9.22230 | -1.29820|
| H         | 1.00900 | 9.18120 | -3.13990|
| H         | -0.26700| 7.08260 | -3.59140|
| H         | 0.01470 | 5.12870 | -2.15800|
| H         | 2.88820 | 1.73460 | -1.50620|
| H         | 5.27160 | 1.58990 | -2.07860|
| H         | 7.47260 | 0.65050 | -1.65170|
| H         | 8.94310 | -0.94740| -0.46530|
| H         | 9.24630 | -2.58340| 1.29830 |
| H         | 8.33820 | -3.97210| 3.14040 |
| H         | 5.88220 | -3.95240| 3.59210 |
| H         | 4.36900 | -2.68510| 2.15830 |
| H         | 1.09550 | -5.39630| 2.07880 |
| H         | -0.16060| -3.36560| 1.50620 |
| H         | 5.06870 | -7.42880| 0.46490 |
| H         | 2.96520 | -6.89030| 1.65170 |
| H         | 6.65260 | -6.92140| -1.29940|
| H         | 7.44510 | -5.46410| -3.14190|
| H         | 6.26480 | -3.31010| -3.59320|
| H         | 4.43280 | -2.57700| -2.15840|
| H         | 0.05830 | -3.36990| -1.50420|
| H         | -1.25880| -5.36180| -2.07590|
| H         | -3.17330| -6.79780| -1.64870|
| H         | -5.29250| -7.27140| -0.46230|
| H         | -6.86080| -6.71500| 1.30130 |
| H         | -7.60930| -5.23310| 3.14260 |
| H         | -6.36440| -3.11560| 3.59280 |
| H         | -4.51030| -2.43960| 2.15850 |
| H         | -5.22190| 1.75060 | 2.07620 |
| H         | -2.83500| 1.82260 | 1.50450 |
| H         | -8.96820| -0.67440| 0.46210 |
| H         | -7.45030| 0.87820 | 1.64890 |
| H         | -9.32030| -2.30050| -1.30170|
| H         | -5.99830| -3.77210| -3.59330|
| H         | -4.44770| -2.55170| -2.15850|
| H         | -8.45400| -3.71640| -3.14320|
