

Buckybowl Synthesis | Hot Paper |

2,7,11,16-Tetra-*tert*-Butyl Tetraindenopyrene Revisited by an “Inverse” Synthetic ApproachSven M. Elbert,^[a] Anika Haidisch,^[a] Tobias Kirschbaum,^[a] Frank Rominger,^[a] Ute Zschieschang,^[b] Hagen Klauk,^[b] and Michael Mastalerz*^[a]

Abstract: A new synthetic route to tetraindenopyrene (TIP)—a bowl-shaped cut-out structure of C_{70} —is reported. The key step in this approach is a fourfold palladium-catalyzed C–H activation that increases the yield more than 50 times in comparison to the approach originally described by Scott and co-workers. Besides examination of its optoelec-

tronic properties and study of its aggregation in solution, TIP was also re-investigated by dispersion-corrected DFT methods, which showed that dispersion interactions significantly increase the bowl-to-bowl inversion barrier. Furthermore, TIP was used as a semiconductor in p-channel thin-film transistors (TFTs).

The discovery of fullerene C_{60} in 1985^[1] stimulated chemists to synthesize this molecule,^[2] other fullerenes or cut-outs thereof—the so called buckybawls.^[3] Buckybawls have interesting properties themselves, but have also been used for the bottom-up synthesis of fullerenes, for example, by flash vacuum pyrolysis.^[4] Besides corannulene,^[5] sumanene^[6] is the simplest substructure of C_{60} and therefore it is not surprising that these two compounds are the most frequently studied.^[3a] In contrast to C_{60} -related buckybawls, similar approaches to compounds representing substructures of C_{70} (Figure 1) are much rarer.^[7] In this respect, Ku’s $C_{38}H_{14}$ and $C_{40}H_{14}$ bowls are among the largest realized so far, with bowl depths of up to 2.33 Å.^[8] Other substructures of C_{70} ^[9] such as rubicenes^[10] or dibenzorubicenes show smaller bowl depths of 1.68 Å^[10b] or twisted^[10a,11] conformations in the solid state. Some of these molecules have been employed as the semiconductor in p-channel thin-film field-effect transistors, with a maximum reported charge-carrier mobility of $1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^[11]

Another substructure of C_{70} is tetraindenopyrene (TIP, 2, Figure 1), which had been the subject of theoretical investiga-

tions by Havenith et al.^[12] and was later synthesized by Scott and co-workers.^[13] The key step of Scott’s TIP synthesis was a quadruple Pd-catalyzed direct arylation of pyrene 1, which provides a yield of only about 0.5% of TIP 2. In the same publication, a one-pot procedure from 1,3,6,8-tetrabromopyrene and 2-bromophenyl boronic acid was described, but yields were again in the range of 0.5%.^[13] Despite the very low yield of the cyclization step, the photophysics of TIP 2 were thoroughly investigated at that time. Based on these properties, the authors suggested that TIP may be a potential candidate for organic electronics or materials chemistry, such as long wavelength dyes for special high-temperature applications. Very recently,

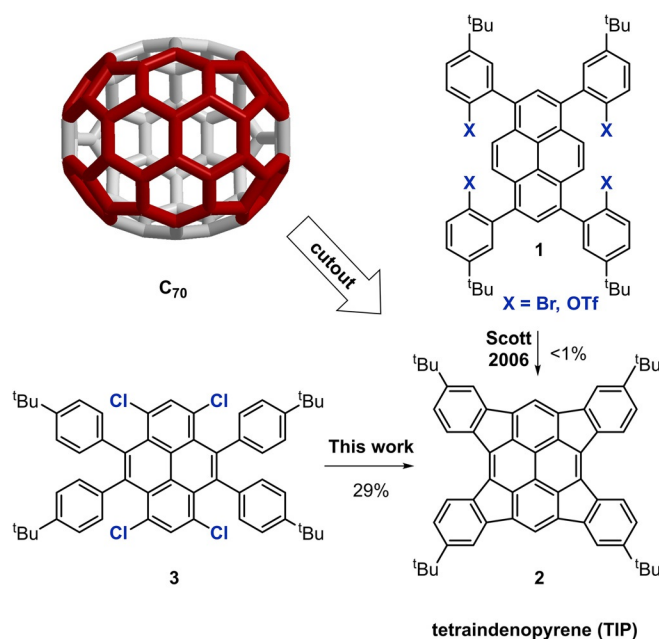


Figure 1. Top left: structure of C_{70} with tetraindenopyrene (TIP) 2 highlighted in red. Right: synthetic approach by Scott,^[13] bottom: this work.

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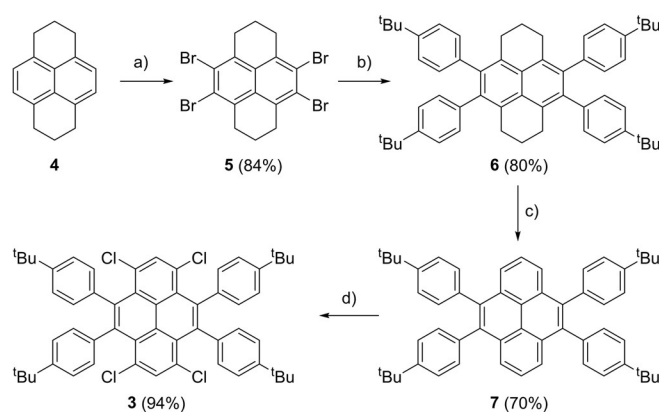
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the synthesis of a structurally related tetra-*n*-octyl TIP by an alumina-mediated HF elimination was reported.^[14] Unfortunately, neither full characterization nor detailed discussion on photophysical or electrochemical properties were included. It is known that the K region of pyrene has a substantial olefin character, and thus the C–H activation may occur by a Heck coupling mechanism, rather than by a C–H activation in which the hydrogen is abstracted from a benzene ring.^[15] Therefore, we developed an alternative approach towards TIP **2** based on C–H activation of tetrachloropyrene **3** (Figure 1).^[16]

The synthesis of pyrene derivative **3** was described previously, starting from pyrene in six consecutive steps.^[16,17] We developed a different synthetic route for **3**, starting from the commercially available hexahydropyrene **4** (Scheme 1) which was selectively fourfold-brominated to **5** and isolated in 84% yield by simple filtration.^[16] Subsequent Suzuki–Miyaura cross-coupling under Fu conditions (Pd₂dba₃, HPtBu₃BF₄) and oxidation of the unsaturated propylene tethers by DDQ gave pyrene **7** in 56% yield over two steps (for details, see the Supporting Information).

The next step was the tetrachlorination of pyrene **7**, which was achieved with a slight excess (4.5 equiv) of *N*-chlorosuccinimide (NCS) in chloroform to obtain **3** in 94% yield (Scheme 1). It is worth mentioning that the chlorination was described previously using a large excess (> 50 equiv) of sulfur-ylchloride.^[16] With the modified synthetic route described here, pyrene derivative **3** can be synthesized in just four steps from commercially available hexahydropyrene **4** in an overall yield of 44%. Furthermore, no purification by column chromatography is required, allowing the synthesis of **2** on gram scale. In comparison, the previously described synthetic route started from pyrene with an overall yield of 4% in six steps and required two steps of purification by column chromatography.^[16–17,19]



Scheme 1. Synthesis of tetrachloro tetraaryl pyrene **3**. a) Br₂, Fe, CH₂Cl₂, 80 °C, 30 min; b) 4-*t*BuPhB(OH)₂, 8 mol% Pd₂dba₃, 30 mol% HPtBu₃BF₄, THF, K₂CO₃ aq (1 M), 80 °C, 16 h; c) 3 equiv DDQ, toluene, 130 °C, 4 h; d) NCS, CHCl₃, 80 °C, 42 h.

All compounds were fully characterized (see the Supporting Information). By vapor diffusion of *n*-pentane into saturated solutions of **5** and **6** in dichloromethane, crystals of sufficient quality for single-crystal X-ray diffraction analyses were obtained (Figure 2). Tetrabromide **5** crystallized in the orthorhombic space group *Pnna* with *Z*=4. The crystal packing is driven by halogen bonding between two bromides with $d_{\text{C-Br}\cdots\text{Br}}=3.63$ Å and dispersion interactions of the bromides with the aliphatic hydrogen ($d_{\text{C-H}\cdots\text{Br}}=3.08\text{--}3.36$ Å, Figure 2 a), forming two-dimensional sheets.^[20] The distance between adjacent sheets is dominated by Br– π interactions ($d_{\text{Br}\cdots\pi}=3.63$ Å),^[21] and these layers are twisted by 16.0° with respect to each other (Figure 2 b, c). Tetraaryl hexahydropyrene **6** crystallized in the triclinic space group *P*-1 with *Z*=2 (Figure 2 d). The molecules interact only by weak dispersion interactions of the pe-

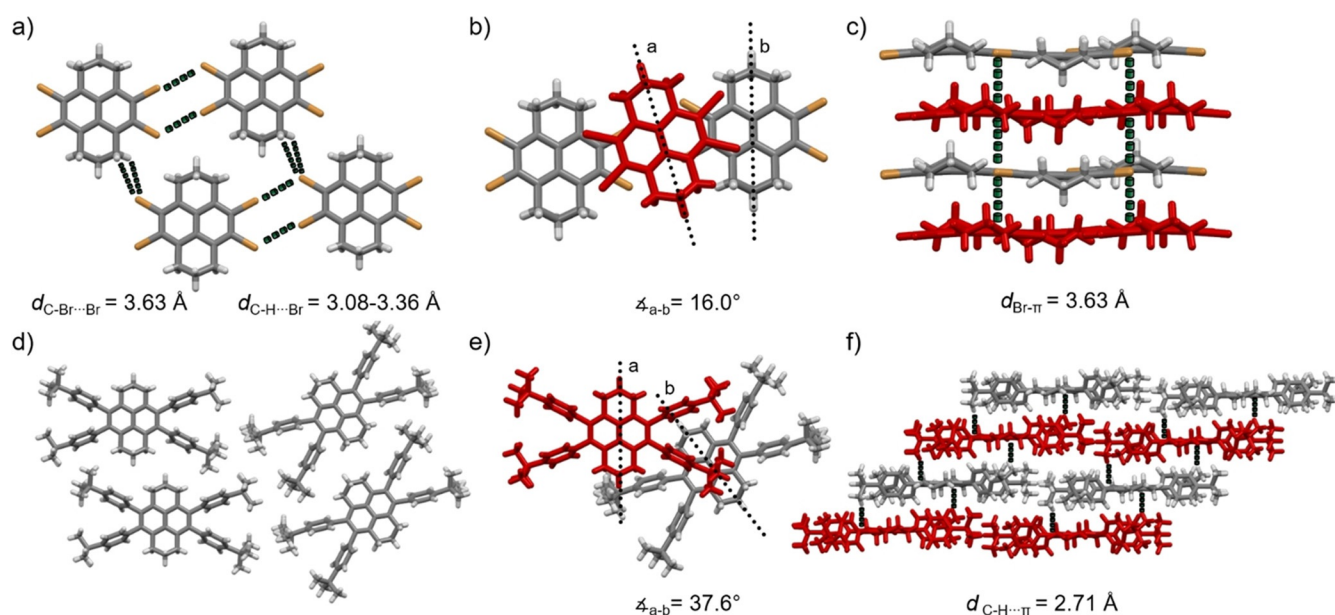
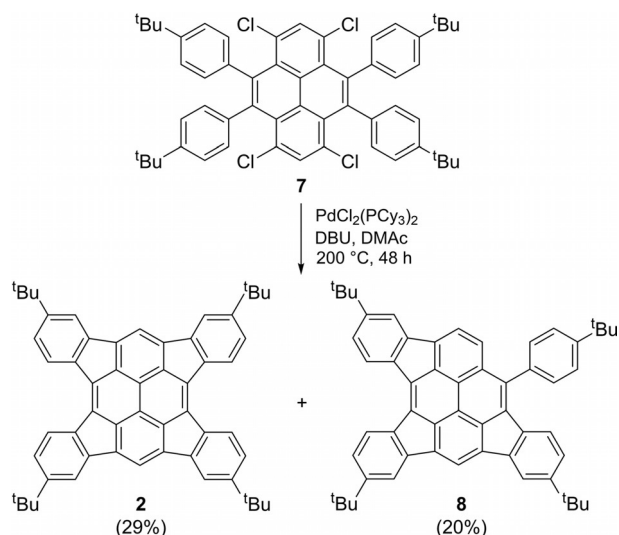


Figure 2. Single-crystal X-ray structures of tetrabromohexahydropyrene **5** (top) and tetraarylhexahydropyrene **6** (bottom) as stick models.

ripheral *tert*-butyl groups with the central naphthyl subunits (Figure 2e).

For the final cyclization by palladium-catalyzed direct arylation under C–H activation, typical reaction conditions ($\text{PdCl}_2(\text{PCy}_3)_2$, DMAc, 200 °C, 48 h)^[22] were used to give the targeted TIP **2** in 29% yield, along with the threefold-cyclized product **8** in 20% yield (Scheme 2). We also performed the cyclization using a wide range of conditions (e.g., various concentrations, solvents, temperatures, duration, alternative Pd sources, alternative bases), but did not obtain greater than 29% yields for **2** nor a higher ratio between the yields for **2** and **8**.



Scheme 2. Synthesis of tetraindenopyrene **2** by C–H activation.

The two compounds can be distinguished by ^1H NMR spectroscopy. Whereas TIP **2** shows four clearly defined signals between $\delta = 7.0$ and 7.5 ppm (corresponding exactly to the previous report^[13]), trindenopyrene **8** shows a more complex signal pattern consisting of 14 signals (two signals overlap at 7.8 and 7.7 ppm) between $\delta = 6.9$ and 8.2 ppm (Figure 3 bottom). Mass spectrometry shows a molecular ion peak for **2** of m/z 722.495 (m/z calcd for $\text{C}_{56}\text{H}_{50}^+$: 722.391), which is two mass units smaller than that of triindenopyrene **8** (m/z calcd for $\text{C}_{56}\text{H}_{52}^+$: 724.407 found: 724.484), consistent with the missing C–C bond.

TIP **2** showed a strong concentration dependence ($c = 0.10$ – 3.08 mM) of the chemical shifts in the ^1H NMR spectra in CD_2Cl_2 (Figure 4), which is indicative of strong π – π -stacking.^[23] At room temperature, protons H^b ($\Delta\delta = 0.37$ ppm) and H^c ($\Delta\delta = 0.19$ ppm) are more weakly influenced than H^a ($\Delta\delta = 0.92$ ppm) and H^d ($\Delta\delta = 0.63$ ppm), because H^b and H^c are sterically shielded by the adjacent *tert*-butyl group against stacking.

Assuming infinite π -stacks, the averaged association K_E was determined to be $2.45 \times 10^3 \pm 0.77 \times 10^3 \text{ M}^{-1}$ ($\Delta G = -19.0 \text{ kJ mol}^{-1}$) at 293 K by a least-squares curve fitting of the infinite (isodesmic) association model (for details see the Supporting Information).^[23a,24] This association constant is much

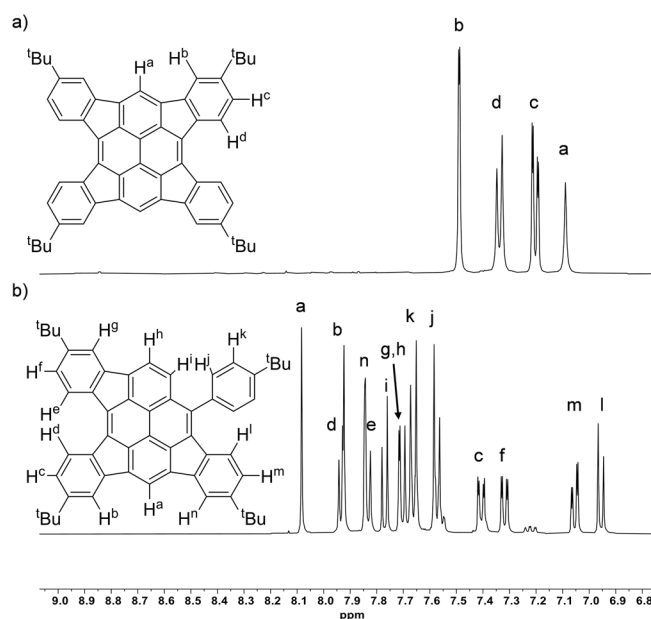


Figure 3. ^1H NMR spectra (400 MHz) of a) TIP **2** and b) trindenopyrene **8** in CD_2Cl_2 at room temperature.

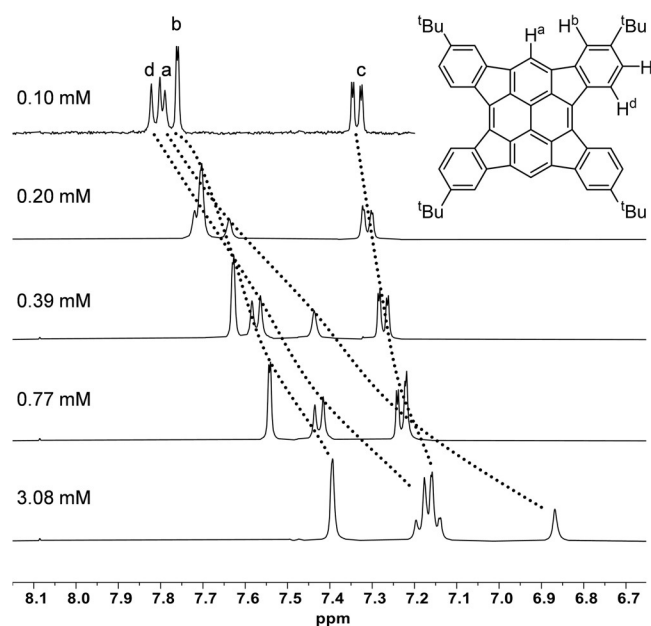


Figure 4. ^1H NMR spectra (400 MHz) of TIP **2** in CD_2Cl_2 at concentrations between 0.10 and 3.08 mM at 293 K.

higher than values reported, for example, for hexabenzocoronene-based thiophene dendrimers (K_E up to 710 M^{-1} in CDCl_3)^[25] and within an order of magnitude of values reported for various perylene- and naphthalene bisimides.^[24d] From measurements performed at temperatures ranging from 243 to 293 K, we determined $\Delta H = -15.8 \text{ kJ mol}^{-1}$ and $\Delta S = 11.9 \text{ J mol}^{-1} \text{ K}^{-1}$ from a van't-Hoff plot; this suggested that the aggregation in solution is driven by both enthalpy and entropy.^[26] The strong aggregation tendency is also reflected by a moderate solubility of **2** in CH_2Cl_2 of $(4.00 \pm 0.63) \text{ mg mL}^{-1}$. At-

tempts to grow single crystals from various solvents produced needle-shaped crystals, which unfortunately could not be structurally refined by X-ray diffraction.

TIP **2** was revisited by theoretical calculations. Scott mentioned that the TIP has a bowl-shaped structure.^[12,13] However, only the bowl-to-bowl inversion barrier calculated by DFT (B3LYP/6-31G*) was discussed, and no further details, such as geometrical parameters or energy levels of frontier molecular orbitals, were provided (see also the Discussion below).^[14] To obtain further insights into the structural details of TIP **2**, dispersion-corrected (D3)^[27] DFT methods (B3LYP/6-311G(d,p)) were used to calculate molecular properties. It was found that the input geometry (MM2 optimized models) is crucial to the outcome of the DFT optimization. Starting from a planar input, the DFT optimization using ultra-tight convergence criteria also produced a planar geometry. A frequency analysis of the result shows an imaginary frequency with $15.5i\text{cm}^{-1}$, which is indicative of a transition state. A second optimization, this time performed with an already contorted input, resulted in a bowl-shaped structure that no longer shows an imaginary frequency; this indicates that it is a realistic energy minimum (Figure 5). The bowl depth is 0.69Å (if measured to the original 2,7-positions of the pyrene) or 1.44Å (maximum bowl depth) and thus similar to the bowl depth of dibenzorubicene (1.68Å).^[10b] The dispersion-corrected calculations gave a greater bowl depth than those performed without the D3 correction term (1.18Å); this result deviates by about 20%(!), thus indicating that dispersion has a significant effect in stabilizing a contorted structure. The *tert*-butyl groups do not contribute substantially to the curving by dispersion interactions (see the Supporting Information).

Based on the dispersion-corrected model, the bowl-to-bowl inversion barrier was calculated to be 6.47kJ mol^{-1} ($\Delta G =$

11.9kJ mol^{-1} , Figure 6). This is substantially higher than without dispersion correction (2.99kJ mol^{-1}) and even higher than the previously published value (1.38kJ mol^{-1}).^[13] Although the estimated inversion barrier is higher, it still means that TIP **2** fluctuates 51 billion times per second between the bowl-shaped minima, much too fast to be determined by variable-temperature NMR measurements. In comparison, corannulene shows an experimentally determined inversion rate of 200 000 per second at room temperature with a corresponding inversion barrier of $\Delta^\ddagger G = 43 \pm 1\text{kJ mol}^{-1}$ ($10.2 \pm 0.2\text{kcal mol}^{-1}$).^[2]

Additional information on the electronic structure of TIP **2** were obtained by AICD^[28] and NICS calculations (HF/6-31+G(d), Figure 5). The outer benzene rings (A) show typical aromatic character with comparable NICS(−1) and NICS(+1) values of -8.8 and -8.7 . NICS(−1) is the concave and NICS(+1) the convex side of the bowl. Aromaticity is also observed for the D-rings (NICS(−1) = -11.7 and NICS(+1) = -7.3 ,

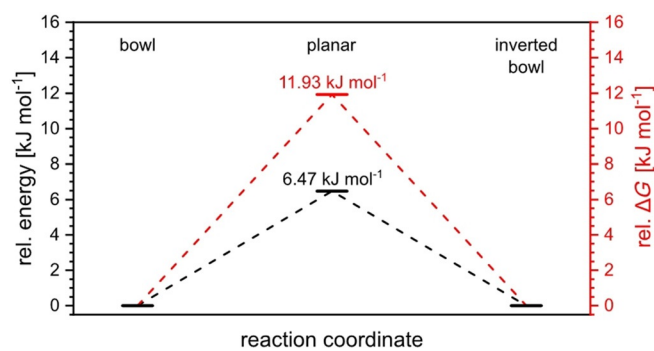


Figure 6. Inversion process of **2** via a planar transition state with the calculated difference in energy (black) and free enthalpy (red) derived from DFT calculations (B3LYP/6-311G(d,p)).

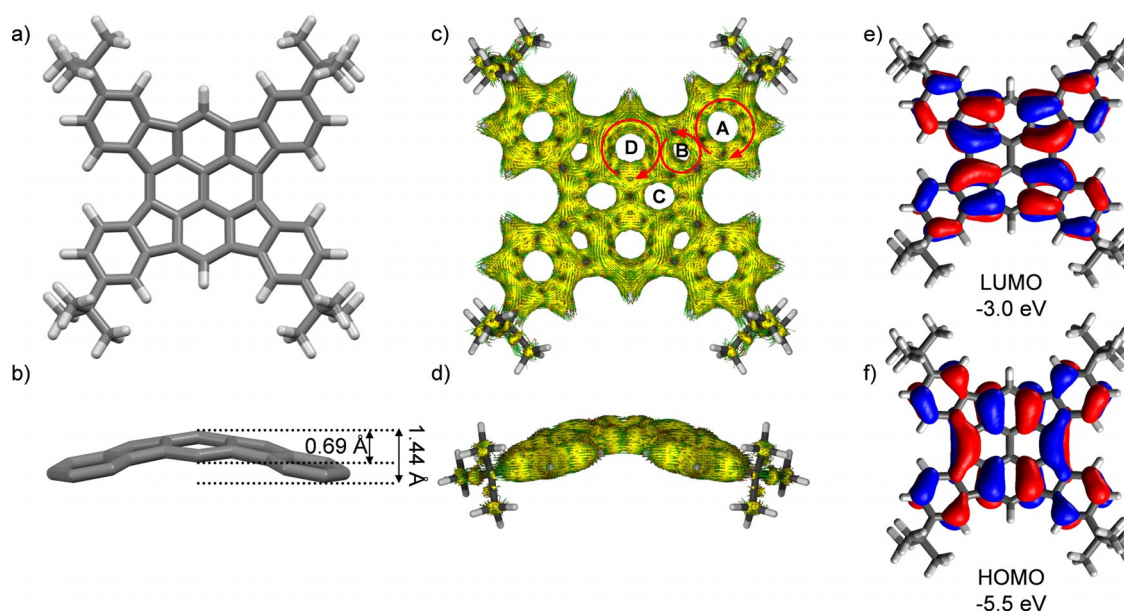


Figure 5. Geometry-optimized model (B3LYP/6-311G(d,p)) of the bowl-shaped TIP **2**. a) Top view. b) side view. AICD plots (HF/6-31+G(d)) of **2** from c) the top/concave side with the magnetic field pointing out of the paper plane and red arrows indicating the direction of the ring current. d) Side view. Canonical MOs of **2** (B3LYP/6-311G(d,p)) with the corresponding orbital energy. e) LUMO; f) HOMO. All calculations were corrected for dispersion (D3).

due to the higher electron density on the bowl's concave side. As known from unsubstituted pyrene,^[12] the C-ring shows smaller aromaticity, with NICS(−1) = −5.3, and here the curvature has by far the greatest influence on the virtual chemical shift, with NICS(+1) = −0.6. The five-membered B-rings are nearly nonaromatic, with NICS(−1) = 1.3 and NICS(+1) = 3.7, and with a tendency toward antiaromatic character, similar to PAHs with fused five-membered rings such as corannulene^[29] or others.^[30] The ring currents derived by AICD calculations (see red arrows in Figure 5c) are in accordance with the trends observed by the NICS calculations.

The DFT-calculated energies of the FMOs are $E_{\text{HOMO, DFT}} = -5.5$ eV and $E_{\text{LUMO, DFT}} = -3.0$ eV (Figure 5e and f). Although no oxidation was recorded within the redox window of the solvents employed (CH_2Cl_2 and *o*-DCB) at anodic potentials, two quasireversible reduction potentials were found in both these solvents (Figure 7). In CH_2Cl_2 , the reduction potentials are $E_{\text{red, 1}}^{1/2} = -1.41$ V and $E_{\text{red, 2}}^{1/2} = -1.74$ V. In *o*-DCB the two reduction peaks were found at slightly lower potentials ($E_{\text{red, 1}}^{1/2} = -1.48$ V and $E_{\text{red, 2}}^{1/2} = -1.84$ V). The first reduction potentials are higher by about 0.3–0.4 V compared to [60]PCBM ($E_{\text{red, 1}}^{1/2} = -1.08$ V) and [70]PCBM ($E_{\text{red, 1}}^{1/2} = -1.09$ V).^[31] Making a commonly used assumption, the electron affinity can be estimated as $EA = -E_{\text{red, 1}}^{1/2} + 4.8$ eV,^[32] corresponding to $EA = -3.46$ eV in CH_2Cl_2 and $EA = -3.42$ eV in *o*-DCB.

The calculated and experimentally determined FMOs suggest that TIP 2 is potentially interesting for organic electronics applications, both as an electron- and as a hole-conducting semiconductor. Initial experiments using 2 in thin-film transistors (TFTs) indicate hole mobilities of $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in TFTs fabricated on silicon substrates and $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in TFTs on flexible polyethylene naphthalate (PEN) substrates and on/off current ratios up to 10^3 measured under ambient conditions (for details, see the Supporting Information).

In summary, we have introduced an alternative synthetic approach to achieve TIP 2 in five consecutive steps and with a 50-fold higher yield both for the final cyclization step (29 vs. 0.5%^[13]) and for the overall synthesis (13 vs. 0.25%). TIP 2 was

revisited by dispersion-corrected DFT calculations, revealing that the bowl-to-bowl inversion barrier is substantially higher than previously estimated. Furthermore, TIP 2 was used to fabricate p-channel TFTs, indicating charge-carrier mobilities up to $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off current ratios of up to 10^3 . To the best of our knowledge, this is the first example of a transistor based on a nonfunctionalized hydrocarbon buckybowl.^[33–35] The possibility of easily scaling up the synthesis of precursor 3 without the necessity for purification by column chromatography will allow us to provide TIP 2 in sufficiently high amounts to explore its chemistry and physics; this is ongoing in our laboratory.

Experimental Section

For experimental details, see the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H activation • organic thin film transistors • polycyclic aromatic hydrocarbons • pyrene • tetraindenopyrene

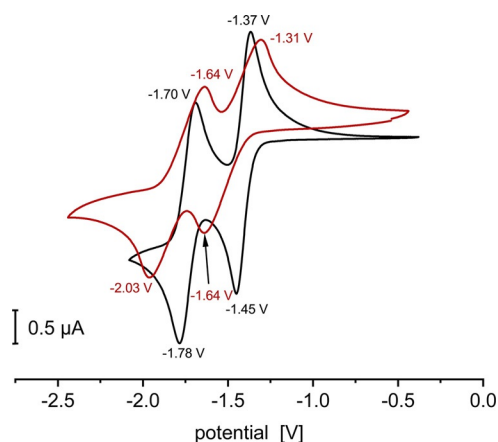


Figure 7. Cyclic voltammograms of TIP 9 in CH_2Cl_2 (black) and *o*-DCB (red), measured at room temperature with a Pt electrode, $n\text{Bu}_4\text{NPF}_6$ (0.1 M) as electrolyte, and Fc/Fc^+ as internal reference (scanning speed: 100 mV s^{-1}).

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