

# ***as*-Indaceno[3,2,1,8,7,6-*ghijklm*]terrylene: a near-infrared absorbing C<sub>70</sub>-fragment**

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Carbon and hydrogen are fundamental components of organic molecules and a fascinating plethora of functions can be generated using these two elements. Yet, realizing attractive electronic structures only by using carbon and hydrogen remains challenging. Herein, we report the synthesis and properties of the C<sub>70</sub> fragment *as*-indaceno[3,2,1,8,7,6-*ghijklm*]terrylene, which exhibits near-infrared (NIR) absorption (up to ca. 1300 nm), even though this molecule consists of only 34 carbon and 14 hydrogen atoms. A remarkably small HOMO–LUMO gap was confirmed by electrochemical measurement and theoretical calculations. Nevertheless, *as*-indacenoterrylene is surprisingly stable despite the absence of peripheral substituents, which contrasts with the cases of other NIR-absorbing hydrocarbons such as biradicaloids and antiaromatic molecules. The low-energy absorption was attributed to the intramolecular charge-transfer from the electron-rich terrylene segment to the electron-deficient *as*-indacenopyrene segment. The results of this study thus offer fundamental insights into the design of hydrocarbons with a small band gap.

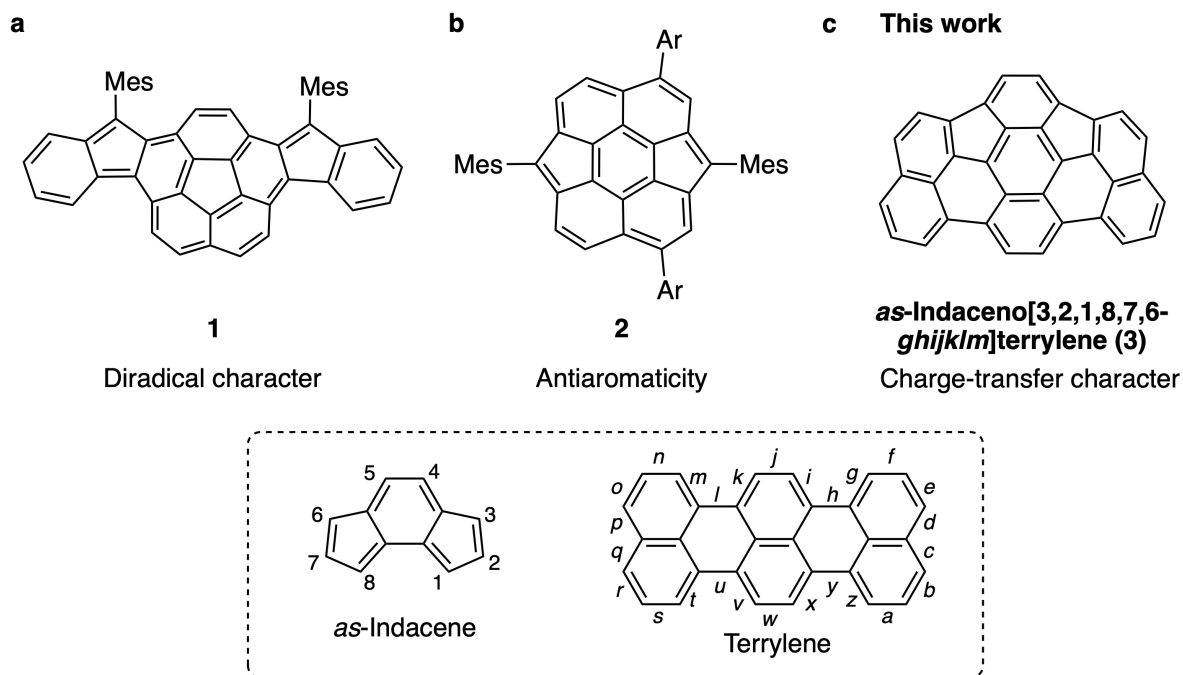
## **Introduction**

Bowl-shaped aromatic hydrocarbons have been actively explored in modern organic chemistry<sup>1–7</sup>. Owing to their structural nonplanarity, these molecules exhibit intriguing characteristics such as high solubility, structural flexibility<sup>8–10</sup>, unique host–guest recognition<sup>11–</sup>

<sup>13</sup> and high electronic conductivity<sup>14,15</sup>. Hence, endowing bowl-shaped aromatic hydrocarbons with unique electronic structures can be considered a promising approach to realize novel functions. Recently, Cao and co-workers have reported indene-fused corannulene derivative **1**, which exhibits a narrow HOMO–LUMO gap due to its diradical nature (Figure 1a)<sup>16</sup>. Such a nonplanar hydrocarbon with a small HOMO–LUMO gap is attractive with regard to potential applications including near-infrared (NIR)-absorbing dyes ambipolar organic semiconductors<sup>17–19</sup>.

During the past three decades, studies on bowl-shaped aromatic hydrocarbons have been related to C<sub>60</sub>-fullerene fragments and their  $\pi$ -extended derivatives<sup>20–25</sup>. C<sub>60</sub> adopts a sphere-like structure with high symmetry ( $I_h$ ), while C<sub>70</sub>-fullerene shows lower symmetry ( $D_{5h}$ ). Consequently, C<sub>70</sub> fragments are inherently diverse, albeit that the hitherto reported C<sub>70</sub> fragments remain limited<sup>26–36</sup>. Among these, especially dicyclopenta[4,3,2,1-*ghi*:4',3',2',1'-*pqr*]perylene (**2**), synthesized by Wu and co-workers, is worth mentioning<sup>36</sup>, as **2** exhibits distinct antiaromaticity and a narrow HOMO–LUMO gap (Figure 1b). Considering that antiaromatic compounds are relatively rare<sup>37–40</sup>, this result highlights that the construction of novel C<sub>70</sub>-fragments may offer a good opportunity to access unique bowl-shaped hydrocarbons with unprecedented electronic structures.

Herein, we disclose the synthesis and properties of C<sub>70</sub> fragment *as*-indaceno[3,2,1,8,7,6-*ghijklm*]terrylene (**3**) (Figure 1c). Surprisingly, **3** exhibits NIR absorption tailing to ca. 1300 nm although it contains only 34 carbons and 14 hydrogen atoms. The low-energy absorption was attributed to the intramolecular charge-transfer from the electron-rich terrylene segment to the electron-deficient *as*-indacenopyrene segment.



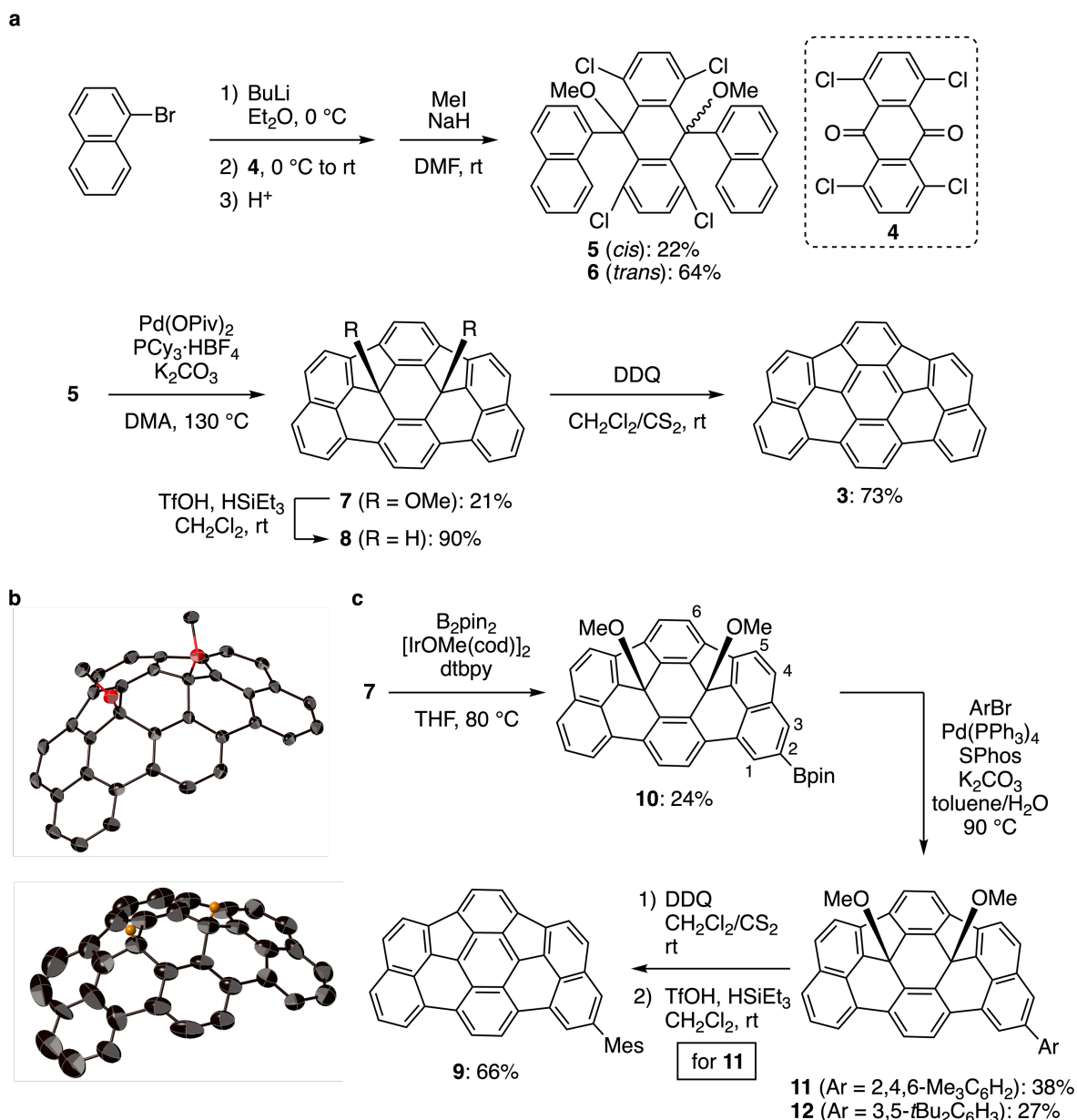
**Figure 1 NIR-absorbing bowl-shaped (anti)aromatic hydrocarbons 1-3. a,** Indene-fused corannulene derivative **1**. **b,** Dicyclopenta[4,3,2,1-*ghi*:4',3',2',1'-*pqr*]perylene (**2**). **c,** *as*-Indaceno[3,2,1,8,7,6-*ghijklm*]terrylene (**3**).

## Results

### Synthesis of *as*-indacenoterrylene **3**

The synthesis of *as*-indacenoterrylene **3** is shown in Figure 2a. The synthetic approach is based on the incorporation of  $sp^3$ -hybridized carbon atoms into the fused  $\pi$ -system to generate the curved structure. The bromine–lithium exchange reaction between 1-bromonaphthalene and butyllithium, followed by the addition of 1,4,5,8-tetrachloroanthraquinone (**4**) afforded the corresponding dinaphthylated diols. The crude mixture was methylated with iodomethane in the presence of sodium hydride, which provided a mixture of *cis*-adduct **5** and *trans*-adduct **6** in 22% and 64% yield (over two steps), respectively. These isomers exhibit different solubility in  $CH_2Cl_2$  and were separated by filtration. The *cis*-isomer **5** engaged in a Pd-catalyzed intramolecular C–H/C–Cl coupling<sup>41</sup> to provide methoxy-substituted *as*-indacenoterrylene **7** in 21% yield, wherein the two five-membered rings are located on the same side. Another isomer, in which the two five-membered rings are located on the opposite side, was not detected. The methoxy group in **7** was transformed to hydrogen using triethylsilane ( $HSiEt_3$ ) and trifluoromethanesulfonic acid ( $TfOH$ )<sup>42</sup>, which afforded **8** in 90% yield. The  $^1H$  NMR signal of the internal hydrogens was observed at 5.91 ppm, which is comparable to that of hydrofullerene  $C_{60}H_2$  (5.93 ppm)<sup>43</sup>. Finally, abstraction of hydrogen from **8** using 1,4-dichloro-2,6-dicyano-*p*-benzoquinone (DDQ) furnished *as*-indacenoterrylene **3** in 73% yield. Although **3** exhibits very low solubility in most common organic solvents, it slightly dissolved in  $CH_2Cl_2/CS_2$ , *o*-dichlorobenzene and *N*-methylpyrrolidone.

The structures of methoxy-substituted *as*-indacenoterrylene **7** and hydrogenated *as*-indacenoterrylene **8** were unequivocally determined by single-crystal X-ray diffraction analysis (Figure 2b). Both **7** and **8** adopt a bowl-shaped structure with two  $sp^3$ -hybridized carbon atoms in the central six-membered ring. Notably, **7** and **8** can be regarded as internally functionalized bowl-shaped aromatics, which have been rarely explored<sup>44–46</sup>. The methoxy groups of **7** are aligned perpendicular to the  $\pi$ -surface, which shows a bowl-depth of 2.10 Å. Unfortunately, the crystal data of **8** is insufficient for a detailed structural analysis due to severe disorder.



**Figure 2 Syntheses and X-ray crystal structures.** **a**, Synthesis of *as*-indacenoterrylene **3**. **b**, X-ray crystal structures of internally methoxy-substituted *as*-indacenoterrylene **7** (top) and internally hydrogenated *as*-indacenoterrylene **8** (bottom). Thermal ellipsoids are drawn at 50% probability and all hydrogen atoms except for the internal hydrogen atoms of **8** are omitted for clarity. **c**, Synthesis of 2-mesityl-*as*-indacenoterrylene **9**.

The <sup>1</sup>H NMR spectrum of *as*-indacenoterrylene **3** in CDCl<sub>3</sub>/CS<sub>2</sub> exhibited seven signals in the range of 7.21–6.78 ppm, supporting a C<sub>s</sub>-symmetric structure. These signals are upfield-shifted by ca. 1 ppm compared to those of other C<sub>70</sub> fragments, except for antiaromatic

dicyclopentaperylene **2**<sup>26–36</sup>. The upfield-shifted <sup>1</sup>H NMR signals are characteristic for  $\pi$ -conjugated systems with narrow HOMO–LUMO gaps<sup>47,48</sup>. The high-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectrum of **3** showed a parent ion peak at  $m/z = 423.1184$  (calcd for C<sub>34</sub>H<sub>14</sub>,  $m/z = 423.1168$  [M+H]<sup>+</sup>), which is in accordance with the expected molecular composition.

As the low solubility of *as*-indacenoterrylene **3** hampered a detailed investigation of the physical properties, we synthesized 2-mesityl-*as*-indacenoterrylene **9** (Figure 2c). The iridium-catalyzed C–H borylation<sup>49</sup> of **7** with bis(pinacolato)diboron furnished 2-borylated **10**. A subsequent Suzuki–Miyaura cross-coupling reaction with 2-bromomesitylene and 1-bromo-3,5-di-*tert*-butylbenzene afforded the arylated products **11** and **12**, respectively. The structure of **12** was determined by a single-crystal X-ray diffraction analysis (Figure S21). Mesityl-substituted derivative **11** was further transformed to 2-mesityl-*as*-indacenoterrylene **9**, which exhibits high solubility in common organic solvents including CH<sub>2</sub>Cl<sub>2</sub>, toluene and tetrahydrofuran.

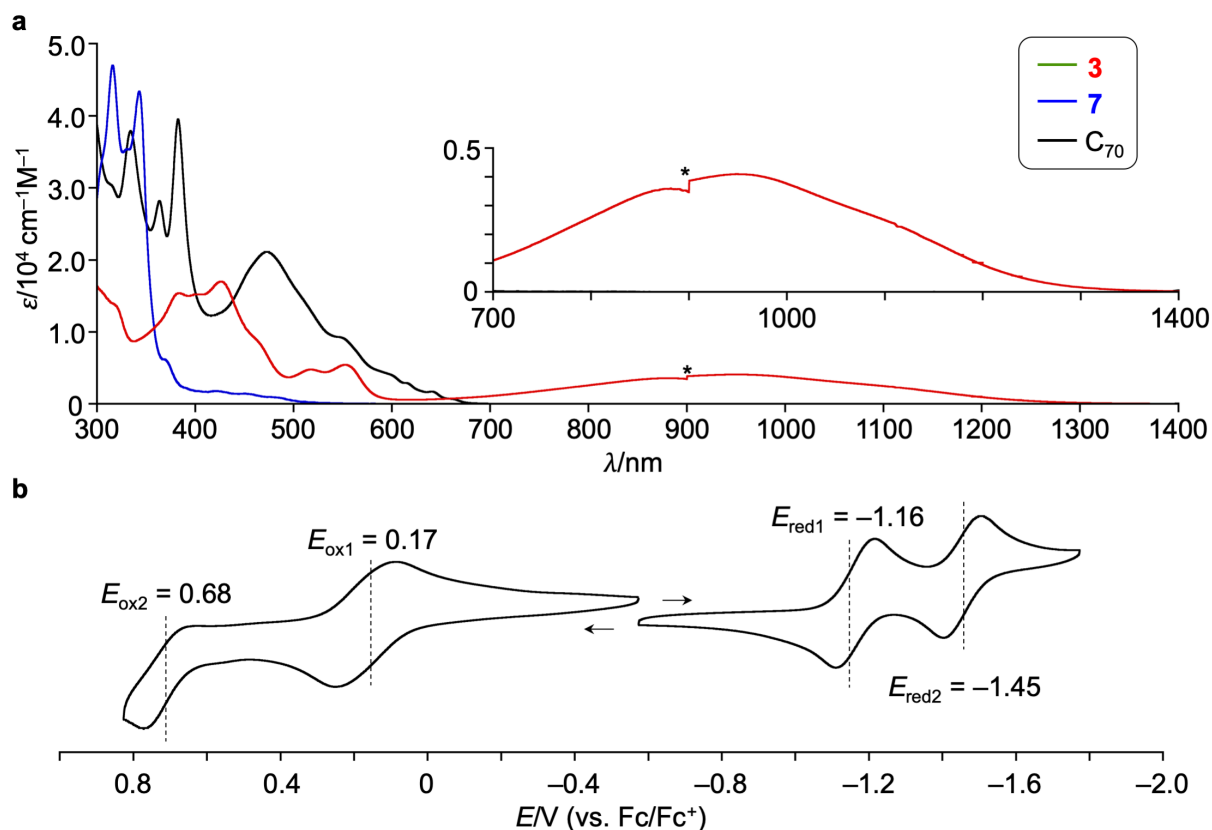
### Bowl-to-bowl inversion

Variable-temperature <sup>1</sup>H NMR spectra of **9** were recorded in CDCl<sub>3</sub> (Figure S22). At 0 °C, the signals that arise from the *ortho*-methyl groups of the mesityl substituent were observed as a pair of singlets with an exchange constant  $\Delta\nu$  of 11.2 Hz. At 35 °C, these singlets coalesced to a single singlet at 2.08 ppm. The observed temperature-dependence can be interpreted in terms of an inversion of the bowl-shaped structure. Based on these results, an inversion barrier of 16.1 kcal mol<sup>–1</sup> at 35 °C was determined<sup>50</sup>. Density functional theory (DFT) calculations at the CAM-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory suggest that this inversion passes through a planar transition state (Figure S23). The calculated activation barrier (15.1 kcal mol<sup>–1</sup>) is comparable to the experimental value.

### Electronic structures

The UV/vis/NIR absorption spectra of **3**, **7** and fullerene C<sub>70</sub> are shown in Figure 3a. Methoxy-substituted **7** exhibits weak absorption bands in the range of 400–520 nm, and the presence of vibrational bands implies structural rigidity. The absorption of **7** is blue-shifted compared to that of fullerene C<sub>70</sub> due to the disrupted conjugation on account of the central sp<sup>3</sup>-hybridized carbon atoms. In sharp contrast, *as*-indacenoterrylene **3** displays a significantly red-shifted absorption with a peak top at 952 nm and a tail to ca. 1300 nm. The optical HOMO–LUMO gap is 1.30 eV. The extinction coefficient of the broad absorption band ( $4.1 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ ) is considerable in comparison to those of the forbidden absorption of indene-fused corannulene derivative **1**<sup>16</sup> and dicyclopentaperylene **2**<sup>36</sup>. As the forbidden S<sub>0</sub>–S<sub>1</sub> transition is a diagnostic feature of antiaromatic molecules<sup>37–40</sup>, the allowed nature of the low-energy absorption of **3** cannot be explained in terms of a potential contribution of antiaromaticity. Interestingly, the absorption tail of **3** is even comparable to that of quarteranthene<sup>51</sup>, which is a zigzag-edge nanocarbon that consists of 56 carbon atoms, and more red-shifted than those of other donor-acceptor systems that consist exclusively of carbon and hydrogen atoms<sup>52–56</sup>. The NIR absorption band of **3** obeys the Lambert–Beer’s law and was matched with that of mesityl-substituted derivative **9** (Figure S24). These results clearly suggest a negligible effect of aggregation on the NIR absorption.

The electrochemical properties of 2-mesityl-*as*-indacenoterrylene **9** were studied by cyclic voltammetry (Figure 3b), using the ferrocene/ferrocenium couple as an external reference, which revealed one reversible oxidation wave at 0.17 V as well as two reversible reduction waves at –1.16 and –1.45 V. The electrochemical HOMO–LUMO gap ( $\Delta E = 1.33 \text{ eV}$ ) was in good agreement with the optical HOMO–LUMO gap. Indene-fused corannulene derivative **1** exhibited redox potentials  $E_{\text{ox1}}$  and  $E_{\text{red1}}$  at 0.33 and –0.81 V, respectively<sup>16</sup>. Dicyclopentaperylene **2** displayed redox potentials  $E_{\text{ox1}}$  and  $E_{\text{red1}}$  at 0.33 and –0.96 V, respectively<sup>36</sup>. The  $\Delta E$  value of **9** is slightly wider than that of **1** and comparable to that of **2**. The redox potentials of **9** are by ca. 0.2–0.3 V positively shifted relative to those of **1** and **2**, which is indicative of a higher electron-donating ability.



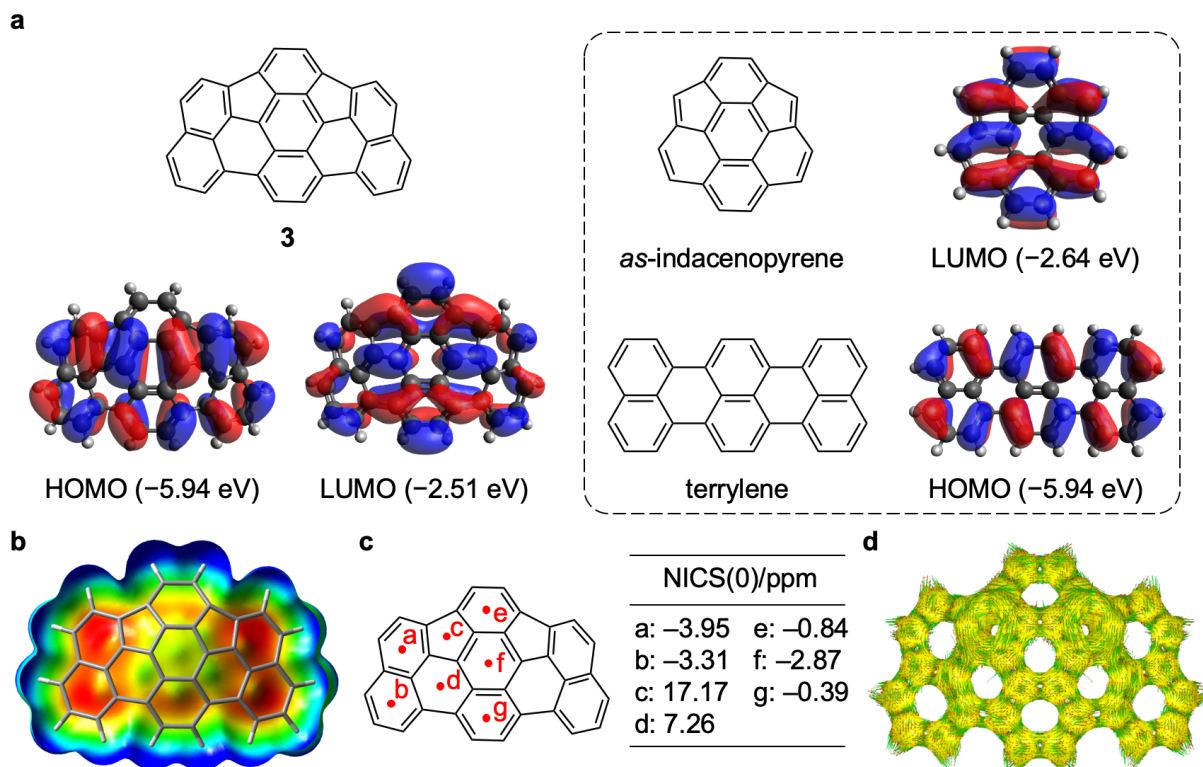
**Figure 3** Narrow HOMO–LUMO gap of *as*-indacenoterrylene. **a**, UV/vis/NIR absorption spectra of **3**, **7** and fullerene  $C_{70}$  in *o*-dichlorobenzene ( $\lambda$ : wavelength;  $\epsilon$ : extinction coefficient). Noise was generated at 900 nm by switching detectors. **b**, Cyclic voltammogram of 2-mesityl-*as*-indacenoterrylene **9** (solvent:  $CH_2Cl_2$ ; supporting electrolyte: 0.1 M  $[Bu_4N][PF_6]$ ; reference electrode:  $Ag/AgNO_3$ ). The second oxidation potential was determined by differential pulse voltammetry.

To evaluate the electronic structure of **3**, DFT calculations were conducted at the CAM-B3LYP/6-311+G(d,p) level of theory. TD-DFT calculations predicted the presence of the HOMO–LUMO transition at 820 nm with an oscillator strength of 0.1226, which is in good agreement with the experimental absorption spectrum (Figure S26). The calculated HOMO and LUMO of **3** are shown in Figure 4a. The HOMO of **3** is delocalized along the longitudinal axis, whose distribution and energy level are almost identical to those of the HOMO of terrylene. In contrast, the LUMO of **3** is mainly located at the centre of the molecule, which resembles the LUMO of *as*-indacenopyrene. The high electron-deficiency of *as*-indacenopyrene can be



attributed to the incorporated non-alternant hydrocarbon segments<sup>57</sup>. These results suggest that the low-energy absorption of *as*-indacenoterrylene **3** is due to the intramolecular charge-transfer character of its HOMO–LUMO transition. This notion is corroborated by the electrostatic potential map of **3**, in which the central *as*-indacenopyrene segment is positively charged relative to the surrounding fused naphthalene units (Figure 4b).

Nucleus-independent chemical shift (NICS)<sup>58,59</sup> calculations and anisotropy of the induced current density (ACID)<sup>60</sup> calculations were conducted for *as*-indacenoterrylene **3** (Figure 4c,d). The NICS(0) values, except for that at the five-membered ring, fall in the range –4.0 to 7.3 ppm. The ACID plot indicates a negligible contribution of the macrocyclic ring current. Furthermore, DFT calculations of **3** at the CASSCF(2,2)/6-31G level of theory furnished a diradical index ( $y = 0.05$ ) that is comparable to that of bisanthene ( $y = 0.07$ ) and much smaller than that of teranthene ( $y = 0.54$ )<sup>51</sup>. These results suggest that the electronic structure of **3** cannot be rationalized satisfactorily in terms of antiaromaticity and diradical character. Indeed, heating an *o*-dichlorobenzene solution of **3** at 100 °C for 12 h under ambient conditions resulted in no distinct spectral change of the absorption, indicating that **3** is remarkably stable despite the absence of peripheral substituents (Figure S28).



**Figure 4** Computational results supporting the charge-transfer character of *as*-indacenoterrylene **3**. **a**, HOMO and LUMO of **3**. Inset: HOMO of terrylene and LUMO of *as*-indacenopyrene. **b**, Electrostatic potential map of **3**. **c**, NICS(0) values of **3**. **d**, ACID plot of **3**.

## Discussion

We have synthesized the  $C_{70}$  fragment *as*-indaceno[3,2,1,8,7,6-*ghijklm*]terrylene **3**. The synthetic concept is based on the generation of curvature by incorporation of  $sp^3$ -hybridized carbon atoms in the fused  $\pi$ -system. The structure was assigned based on NMR spectroscopy and mass spectrometry. The physical properties were probed by UV/vis/NIR absorption spectroscopy, cyclic voltammetry, temperature-dependent NMR analysis and theoretical calculations. Even though **3** contains only 34 carbon and 14 hydrogen atoms, it absorbs in the NIR region up to ca. 1300 nm. This low-energy absorption was attributed to the intramolecular charge-transfer character of the HOMO–LUMO transition, which is due to the coexistence of an electron-rich terrylene segment and an electron-deficient *as*-indacenopyrene segment. The absorption tail of **3** is not only comparable to organic diradicaloid **1** and antiaromatic hydrocarbon **2**, but also more red-shifted than those of other donor–acceptor systems that

consist exclusively of carbon and hydrogen atoms. Nevertheless, *as*-indacenoterrylene **3** exhibits outstanding stability despite the absence of peripheral substituents, which stands in sharp contrast to the behaviour of other NIR-absorbing hydrocarbons such as biradicaloids and antiaromatic molecules. The current study thus offers new design guidelines for curved aromatic hydrocarbons with narrow HOMO–LUMO gaps and all-carbon donor–acceptor systems.

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#### **Additional Information**

**Supplementary information** is available.