Disproportionation reactions are arguably one of the most important classes of organic reactions, especially in the context of coal liquefaction and aromatization, as well as Cannizzaro and biochemical reactions. However, reports on disproportionation reactions of aromatic hydrocarbons remain scarce. Stein and co-workers have reported the disproportionation of 9,10-dihydroanthracene (>350 °C; liquid phase pyrolysis) into tetrahydroanthracene and anthracene.1 Pentacene has also been reported to undergo disproportionation at 320 °C in a horizontal vapor phase deposition furnace to produce 6,13-dihydropentacene tetrahydroanthracene and anthracene derivatives, as well as a detailed investigation into the color of the solid changed from colorless to green. To elucidate the origin of this green material, we investigated the thermally and photolytically induced disproportionation of 6,13-dihydropentacene derivatives into tetrahydroanthracenes and pentacenes results in unique solid-state fluorescence. The fluorescence thereby depends on the molecular structure and the molecular arrangement in the solid state.

The synthesis of \( N,N' \)-bisalkyl-6,13-dihydropentacene \([2,3:9,10] \)bis-carboxyimides \( 3a-c \) is outlined in Scheme 1. We have previously reported the synthesis of key starting material 6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid (1).\(^*\) Tetra-carboxylic acid 1 was converted into the corresponding anhydride (2) in good yield using a modification of the procedure reported by Qian and co-workers.\(^*\) \( N,N' \)-Bisallyl-6,13-dihydropentacene\([2,3:9,10] \)bis-carboxyimides \( 3a-c \) were then obtained in 20–64% yield by stirring anhydride 2 under reflux in the presence of the corresponding amines. The structure of the obtained dihydropentacene bisimides was confirmed by \(^1H\) and \(^13C\) NMR spectroscopy, IR spectroscopy, FAB mass spectrometry, and elemental analysis. The \(^1H\) NMR spectrum of 3a in CDCl\(_3\) shows a singlet at 4.36 ppm, which was assigned to the central ring of dihydropentacene. In the aromatic region, two singlets appear at 8.03 and 8.23 ppm, which were attributed to the naphthalene ring. The \(^13C\) NMR NMR spectrum of 3a displays 13 signals, including five aromatic carbon atoms (123.5, 128.0 \times 2, 134.4, 138.4, and 168.3 ppm) for the naphthalene ring, one carboxyl carbon atom (186.3 ppm), and one sp\(^3\)-hybridized carbon atom of the central ring (38.5 ppm). In general, the spectra of 3a-c are very similar.

Subsequently, we examined the disproportionation reaction of dihydropentacene 3a in the solid state (Scheme 2). Interestingly, upon heating solid 3a from room temperature to 230 °C, the color of the solid changed from colorless to green. To elucidate the origin of this green material, we investigated the absorption features of a thin film of 3a before and after heating (250 °C; 3 h). In the difference spectrum of 3a (Fig. 1), the positive absorption bands at 523, 560, and 611 nm were very similar. The position of absorption bands at 523, 560, and 611 nm were very similar.
attributed to an expansion of the \( \pi \)-conjugated system. A comparison with the absorption spectrum of independently synthesized \( \text{N},\text{N}’ \)-bispentylpentacene[2,3:9,10]biscarboxyimide (4a) revealed very similar features. The formation of pentacene derivative 4a was also confirmed by \( ^1 \text{H} \) NMR spectroscopy (Fig. S1†). After heating (250 °C; 40 min), the main signals were assigned to the starting material (3a), and the new signals suggested a conversion <7%. The \( ^1 \text{H} \) NMR spectrum in CDCl\(_3\) showed three singlets at 8.50, 8.94, and 9.12 ppm, which were assigned to the protons attached to the pentacene core, respectively. Moreover, three singlets for aromatic protons (8.06, 8.22, and 8.39 ppm) and two singlets for methylene protons (4.27 and 4.81 ppm) were observed for tetrahydropentacene derivative 5a. Upon exposure to air, the signals of 4a disappeared and two singlets at 8.56 and 9.14 ppm appeared, which were assigned to pentacene quinone 7a, i.e., the oxidation product of pentacene 4a (Fig. S2†). An integral 5a : 7a ratio of 1 : 1 was estimated. These results strongly indicate that the thermal reaction of dihydropentacene 3a affords pentacene 4a and tetrahydropentacene 5a (Scheme 2).

Moreover, we discovered that \( \text{N},\text{N}’ \)-bisalkyl-6,13-dihydropentacene[2,3:9,10]bis-carboxyimide 3a exhibits solid-state fluorescence (Fig. 2); under illumination with UV light \( (\lambda_{ex} = 365 \text{ nm}) \), bright blue fluorescence was observed. Interestingly, upon heating 3a in solid state from room temperature to 230 °C, the color of the apparent fluorescence gradually changed from bright blue to yellow and then red (Fig. 2a). Such phosphorochromaticity was observed for both film and crystal-line samples (Fig. 2b), and the original color was not recovered even after cooling to room temperature. The differential scanning calorimetry (DSC) cooling and heating curves of 3a showed no peaks between room temperature and 270 °C (Fig. S3†). In the case of 3b and 3c, similar fluorescence color changes were observed, while the crystal appearance changed from transparent to opaque. Polarized optical microscopy images revealed rough and cracked surfaces of the crystals of 3b and 3c after heating (Fig. S4†).

We also observed significant changes in the fluorescence spectra of a thin film of 3a with increasing temperature (Fig. S5†). The intensity of the fluorescence of the naphthaleneimide chromophore (300–550 nm) decreased with increasing temperature, while the intensity of the new fluorescence band at 638 nm, which was assigned to a pentacene chromophore, increased. The decaying emission of the naphthaleneimide skeleton may be explained in terms of an energy transfer from 3a to 4a.†

Fig. S6† shows the concentration-dependent emission spectra of 3a in CHCl\(_3\). At a concentration of 1.9 \times 10^{-4} \text{ M}, a monomer emission band from the naphthaleneimide moiety was observed at 390 and 400 nm \( (\lambda_{ex} = 280 \text{ nm}) \). Upon increasing the concentration of 3a beyond 7.7 \times 10^{-3} \text{ M}, the fluorescence intensity of the naphthaleneimide moieties decreased and two new excimer emission bands emerged at approximately 440 and 460 nm with growing intensity. These results indicate that the solid-state fluorescence at 440 nm does not correspond to monomer emission, but to aggregate emission.

In order to determine the molecular conformation in the crystals and rationalize the observed reactivity, a single-crystal X-ray diffraction analysis was carried out (Fig. 3). Depending on the solvent, two different crystalline structures were identified in the case of 3a. A structural analysis of single crystals of 3a–c grown from benzonitrile solutions revealed a planar central six-membered ring of the dihydropentacenes (Fig. 3a, and S8†). The bond angle sums of the central six-membered rings are close to 720°. Numerous hitherto reported crystal structures are characterized by flattened boat conformations for dihydroanthracene and dihydropentacene derivatives, whereas the preferred conformation of dihydroaromatics should be a planar according to a theoretical study.† In fact, there are a few crystallographic reports on dihydroanthracene\(^{13}\) and dihydropentacene\(^{14}\) skeletons with a planar geometry. In contrast, the structural analysis for crystals of 3a grown from

**Scheme 2** Disproportionation reaction of dihydropentacene 3a and decomposition of pentacene derivative 4a.

![Scheme 2](image)

**Fig. 1** The absorbance difference spectrum of a thin film of 3a before and after the heating.

![Fig. 1](image)

**Fig. 2** (a) Apparent fluorescence color change of a 3a film with the increasing temperature. (b) Apparent fluorescence color change of crystals of 3a.
a THF solution revealed a V-shaped dihydropentacene skeleton with a bent central six-membered ring 3a(v).

The energy difference between the planar and V-shaped conformers was examined using density functional theory (DFT) calculations on model compound 3, which bears H atoms instead of alkyl chains. The V-shaped conformer 3(v) is by 4.0 kcal mol\(^{-1}\) thermodynamically more stable than the planar conformer 3(\text{planar}). These results suggest a small energy difference between the two conformers. Consequently, the solid-state structure of 3a is most likely determined by packing forces in the crystal.

Interestingly, the phosphorochromaticity changes in the solid state were also triggered by photoirradiation (>300 nm); however, the reaction was limited to the surface of the specimen. The phosphorochromaticity switching rate was sensitive to the substituents on the dihydropentacene. Upon photoirradiation of solids 3a(\text{planar}) and 3b \((\lambda_{ex} > 300 \text{ nm}; 1 \text{ h})\), the apparent fluorescence color gradually changed from bright blue to red. In the case of 3(v) and 3c, the apparent fluorescence color did not change, not even after two days of photoirradiation. To clarify the different reactivity of the planar and V-shape conformers of 3a, further DFT calculations were carried out. Fig. 4 shows the relevant Kohn–Sham molecular orbitals for the optimized structures of 3(\text{planar}) and 3(v). Both HOMOs are clearly localized on the C–H bonds of the central six-membered ring and the two naphthalene units. Interestingly, the LUMO of 3(\text{planar}) is notably less localized around the C–H bond of the central six-membered ring than the LUMO of 3(v). These results indicate that the excited state of 3a(\text{planar}) favors the elimination of the C–H protons of the central six-membered ring compared to the case of 3a(v).

To evaluate the differences in photoreactivity depending on the substituents, the molecular arrangements in the crystals were investigated. None of the crystals contained any solvent in the lattice. The distances between the H (from the C–H bonds of the central six-membered ring) and C (from the naphthalene ring of the neighboring molecule) atoms were ca. 3.0 Å (3a), 2.8 Å (3b), and 3.3 Å (3c). The long distance in the crystals of 3c should thus be unfavorable for hydrogen-atom transfer from the C–H bond of the central six-membered ring to the naphthalene ring of the neighboring molecule.

Conclusions

\(N,N^2\)-Bisalkyl-6,13-dihydropentacene[2,3-9,10]bicarboximides 3a–c undergo disproportionation reactions in the solid state. The molecular structure and conformation in the crystals strongly influence the disproportionation reaction. Upon heating or photoirradiation of 3 in the solid state, the fluorescence color gradually changed from bright blue to red. The solid-state fluorescence behavior\(^{35}\) induced by disproportionation may serve as an example for guided molecular engineering, providing fascinating possibilities to tune materials for sensing, as well as optical and thermal recording applications.

Experimental section

Instruments

Unless otherwise stated, all experiments were performed under an atmosphere of argon. Solvents were dried by standard methods and distilled prior to use. CDCl\(_3\) was purchased from Cambridge Isotopes. NMR spectra were recorded on a JEOL JNM AL-300 or a Varian NMR System 600 spectrometer. The \(^1\)H and \(^{13}\)C NMR shifts are given in ppm relative to tetramethylsilane (TMS; \(\delta = 0 \text{ ppm}\)) and referenced internally with respect to the residual proton (CDCl\(_3\); \(\delta = 7.26 \text{ ppm}\)), or the \(^{13}\)C NMR resonance of the solvent (CDCl\(_3\); \(\delta = 77 \text{ ppm}\)). UV-visible spectra were measured on a Shimadzu UV-3150 spectrometer. Emission and excitation spectra were recorded on a Jasco FP-6500 spectrometer, while IR spectra were obtained on a Thermo Nicolet IR Affinity-1 spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60 in air. Wet column chromatography (WCC) was performed using Wakogel C-200. The melting points were determined on a MEL-TEMP micro melting point apparatus and are uncorrected. Reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Chemical Industries Co., Ltd., Kanto Kagaku Co., Ltd., Nacalai Tesque Co., Ltd., and Aldrich Chemical Co. Pentacene-2,3,9,10-tetracarboxylic acid (1) was prepared according to reported procedures.\(^8\)

Synthesis of 2 and 3a–c

Synthesis of 2. Tetraacid 1 (267 mg, 0.59 mmol) was stirred for 3 h at 140 °C in acetic anhydride (50 mL). After cooling to room temperature, the solvent was removed \textit{in vacuo}. The corresponding diacidhydride (2) was obtained as a yellow solid (223 mg, 0.53 mmol, 90%). 2: mp \(> 300 \text{ °C}\); IR (KBr) 893, 1215, 1778, 1836, and 3464 cm\(^{-1}\). The low solubility of 2 prevented the recording of \(^1\)H and \(^{13}\)C NMR spectra.

Synthesis of 3a. A glacial acetic acid solution (30 mL) of 2 (150 mg, 0.357 mmol) and 1-aminohexane (108 mg, 1.07 mmol)
was stirred for 12 h under reflux. After removal of the solvent, the residue was extracted several times with CHCl₃. The organic layers were combined, washed with HCl (5 wt% in water) and brine, before being dried over anhydrous MgSO₄. After filtration and removal of the solvent from the filtrate, the mixture was purified by WCC (CHCl₃) to give 3a (41.9 mg, 0.071 mmol, 20%) as colorless crystals. 3a (n-hexane): mp 250 °C (decomp.); ¹H NMR (300 MHz, CDCl₃): δ 0.88 (brs, 6H), 1.33 (brs, 12H), 1.71 (brs, 4H), 3.74 (t, J = 7.5 Hz, 4H), 4.36 (s, 4H), 8.03 (s, 4H), 8.30 (s, 4H) ppm; C¹³ NMR (75 MHz, CDCl₃): δ 13.9 (q), 27.2 (t), 29.4 (t), 32.0 (s), 123.8 (s × 2), 131.4 (s). Anal. calc’d for C₁₈H₁₈N₂O₄: C, 77.79; H, 6.53; N, 4.77; found: C, 77.59; H, 6.41; N, 4.67.

Synthesis of 3b. A toluene solution (40 mL) of 2 (175 mg, 0.416 mmol) and 1-amino tridecane (839 mg, 4.16 mmol) was stirred for 6 h under reflux using a Dean–Stark trap. After removal of the solvent, the residue was extracted several times with CHCl₃. The organic layers were combined, washed with HCl (5 wt% in water) and brine, before being dried over anhydrous MgSO₄. After filtration and removal of the solvent from the filtrate, the mixture was purified by WCC (CHCl₃) to give 3b (100 mg, 0.139 mmol, 30%) as colorless crystals. 3b (tridecane): mp 250 °C (decomp.); ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, J = 6.0 Hz, 6H), 1.23 (brs, 40H), 1.32 (brs, 40H), 3.72 (t, J = 6.0 Hz, 4H), 4.35 (s, 4H), 8.01 (s, 4H), 8.28 (s, 4H) ppm; C¹³ NMR (75 MHz, CDCl₃): δ 14.1 (q), 22.7 (t), 28.6 (t), 29.2 (t), 29.4 (t), 29.7 (t), 31.8 (t), 31.9 (t), 37.2 (t), 38.2 (t), 123.8 (s × 2), 131.4 (s), 138.5 (s), 161.8 (s) ppm; UV–vis (CHCl₃): λ max 305 (18 000), 365 (9000) nm; IR (KBr) 2956, 2922, 1703, 1701, 1439, 1393, 1360, 1379, 1120, 947, 905, 746, 621, 579, and 480 cm⁻¹. Anal. calc’d for C₃₈H₃₈N₂O₄: C, 78.47; H, 7.21; N, 4.36; found: C, 78.32; H, 7.28; N, 4.30.

X-ray data collection

Single crystals of 3a–c were grown by slow evaporation of saturated solutions of 3a–c in benzonitrile at room temperature. Single crystals of 3a(ø) were grown by slow evaporation of a saturated solution of 3a(ø) in THF at room temperature. The crystals were coated with hydrocarbon oil, mounted on glass fibers, and placed under a cold stream of N₂ in the diffractometer. The intensity data for 3a–c were collected on a Rigaku VariMax diffractometer with a Saturn CCD detector using graphite-monochromated Mo-Kα radiation (λ = 0.71071 Å) up to 2θmax = 50° at 103 K. All structures were solved by Patterson methods (SHELXS-97) and refined by full-matrix least-squares procedures on F² for all reflections (SHELXL-97). All hydrogen atoms were located following AFFIX instructions. All other atoms were refined anisotropically. CCDC-1911683 (3a(planar)), CCDC-1911685 (3a(ø)), CCDC-1911683 (3b), and CCDC-1911686 (3c) contain the supplementary crystallographic data for this paper.

3a(ø): C₁₈H₁₈N₂O₄, MW = 342.36, triclinic, space group P1 (2), α = 9.15765(12) Å, β = 9.6222(12) Å, γ = 122.166(15) Å, V = 1074.5(11) Å³, Z = 1, Dcalc = 1.164 g cm⁻³, μ = 0.094 mm⁻¹, Rp = 0.0616, wR² (all data) = 0.212, T = 103(2) K, GOF = 1.051.

3a: C₁₈H₁₈N₂O₄, MW = 342.36, triclinic, space group P1 (2), α = 9.15765(12) Å, β = 9.6222(12) Å, γ = 122.166(15) Å, V = 1074.5(11) Å³, Z = 1, Dcalc = 1.164 g cm⁻³, μ = 0.094 mm⁻¹, Rp = 0.0616, wR² (all data) = 0.212, T = 103(2) K, GOF = 1.051.

3b: C₃₈H₃₈N₂O₄, MW = 642.81, triclinic, space group P1 (2), a = 7.861(5) Å, b = 8.965(5) Å, c = 14.802(12) Å, α = 78.46(5), β = 84.78(5), γ = 113.33(4), V = 685.7(11) Å³, Z = 1, Dcalc = 1.133 g cm⁻³, μ = 0.079 mm⁻¹, Rp = 0.078, wR² (all data) = 0.1264, T = 103(2) K, GOF = 1.059.

Conflicts of interest

The authors declare no conflicts of interest.

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