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Functionalization of pentacene-5,7,12,14-tetraone with geminal enediyne and 1,3-dithiole groups[†]

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Pentacene-5,7,12,14-tetraone was subjected to selective olefination and cross-coupling reactions to yield a new class of pentacene-based π -conjugated systems functionalized with geminal enediyne and 1,3dithiole groups. The electron donating and accepting effects of enediyne and dithiole groups render these compounds intriguing structural, electronic properties, and redox activities which were systematically investigated by UV-Vis absorption and cyclic voltammetric analyses in conjunction with density functional theory (DFT) calculations. The bis(enediyne)-substituted pentacenedione showed potential application in the preparation of carbon-rich polymeric materials.

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Introduction

Acenes and acenequinones are π -conjugated building blocks widely employed in the field of molecular electronic and photonic materials, owing to their unique structural, redox, and semiconducting properties.^{1–10} Synthetically, the presence of keto groups in acenequinones allows the acene backbones to be functionalized with diverse electronic and redox-active moieties through numerous reactions. Fig. 1 depicts two functionalization routes which have drawn considerable interest in our recent research. First, quinone can undergo Wittigtype olefination to form π -extended tetrathiafulvalene analogues (exTTFs),^{11–13} which have wide applications in chemical sensing,^{14,15} supramolecular guest–host chemistry,^{16–22} photovoltaics,^{23–26} and so forth. Second, the keto groups can be subjected to the Corey–Fuchs reaction to give geminal dihalovinyl intermediates, from which various π -conjugated scaffolds can be installed *via* cross-coupling reactions.^{27–30}

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Many acene-based exTTFs and geminal enediyne derivatives, reported in the literature, have been derivatized from acene-diones (e.g., anthraquinones and pentacenediones) so far.11-13,22,31-35 Acene-polyones however are less utilized precursors because they do not have synthetic access as easy as the diones. Conceptually, derivatization of acene-polyones not only allows more functional groups to be incorporated to attain enhanced and/or unprecedented properties, but also leads to a multitude of structural variations as a consequence of the rich regioselectivity and conformational isomerism involved. Motivated by this consideration, we have recently synthesized a new class of π -extended TTF derivatives (A, Fig. 2) using pentacene-5,7,12,14-tetraone (1) as the precursor.³⁶ To further develop new π -molecular systems from pentacenetetraone, we subsequently adopted an approach of combining geminal enediyne and 1,3-dithiole groups37-39 (see motifs B



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Fig. 2 Derivatizations of pentacene-5,7,12,14-tetraone into π -extended redox-active systems.

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and C, Fig. 2). The enediyne was anticipated to function as an electron-deficient group to modulate the π -electron characteristics and to serve as structural elements for the formation of more extended polymer networks. The following sections describe our detailed investigations on the synthesis and characterization of these new pentacene-based derivatives.

Results and discussion

Synthesis of enediyne and dithiole-functionalized pentacene derivatives 3 and 5

In the synthesis (see Scheme 1), pentacene-5,7,12,14-tetraone (1) was first subjected to the Corey–Fuchs reaction $^{27-30}$ with excess CBr₄ and PPh₃ for 24 hours, affording tetrabromide 2 as a colourless solid in a yield of 60%. It is worth noting that only two of the four keto groups in 1 at the 5- and 12-positions underwent olefination, while the other two remained intact. Such regioselectivity is similar to the nucleophilic substitution of pentacene-5,7,12,14-tetraone with aryl- or ethynyllithiums reported by Yamashita *et al.*²⁴ The C_2 symmetric structure of 2 was clearly evidenced by its ¹H NMR data, where five distinctive signals are seen in the aromatic region and the two chemically equivalent protons on the 6- and 13-positions resonate as a singlet at 8.80 ppm. Tetrabromide 2 then underwent the Sonogashira-Hagihara coupling reaction with excess trimethylsilvlacetylene (TMSA), yielding compound 3 as a yellow solid in 87% yield. Finally compound 3 was reacted with 1,3-dithiole-2thione 4 in P(OEt)₃ at 110 °C to afford compound 5 as a deepred solid in 52% yield.40

Structural and electronic properties of compounds 3 and 5

The molecular structures of compounds 2, 3 and 5 were characterized by NMR, IR and MS analyses. The ground-state geometries of 3 and 5 were modelled by density functional



Scheme 1 Synthesis of enediyne and 1,3-dithiole-functionalized pentacene derivatives 3 and 5.



Fig. 3 Optimized structures of compounds (A) 3 (*trans* conformer), (B) 3 (*cis* conformer), (C) 5 (*trans* conformer), and (D) 5 (*cis* conformer). Calculations performed at the B3LYP/6-31G(d) level of theory. TMS and $SC_{10}H_{21}$ groups were replaced with H atoms to reduce computational expenses.

theory (DFT) calculations and the optimized structures are shown in Fig. 3. For compound 3, two stable conformers were found, namely *trans* and *cis* (Fig. 3A and B) in terms of the orientations of the two enediyne moieties relative to the central pentacene unit. The central pentacene structure of the *trans* conformer shows a zig-zag shape, while the *cis* conformer adopts a curved shape. Energetically, the *cis* conformer is slightly more stable than *trans* by 0.614 kcal mol⁻¹, even though the *trans* has a dipole moment (0.817 Debye) much greater than that of *cis* (0.0005 Debye). The observation of five distinctive aromatic signals in the ¹H NMR spectrum of 3 at room temperature suggests that the *cis* and *trans* conformers are in rapid exchange in the solution phase with a very low energy barrier.

Compound 5 was calculated to have two stable conformers, *cis* and *trans*, as well. However, the *trans* conformer is more stable than *cis* by 2.04 kcal mol⁻¹, which is in consistence with the preference for a minimal dipole moment; that is, the dipole moment of *trans* (0.0024 Debye) is much smaller than that of *cis* (0.746 Debye). The relatively large energy difference between the two conformers of 5 suggests that *trans* is the major conformation for compound 5 in the solution phase at room temperature.

The electronic properties of 3 and 5 were investigated by UV-Vis absorption analysis (Fig. 4). In $CHCl_3$ compound 3



Fig. 4 Normalized UV-Vis absorption spectra of compounds 3 and 5 measured in $CHCl_3$ and as a solid film (5) at room temperature. Inset: Comparison of the normalized low-energy absorption bands in the solution-phase and solid-state UV-Vis spectra.

gives rise to two $\pi \to \pi^*$ absorption bands at 436 nm and 358 nm. The low-energy band is mainly due to HOMO \rightarrow LUMO transition according to time-dependent (TD) DFT calculations (see Table S-1, ESI[†]). Compound 5 in CHCl₃ gives three absorption bands at 516 nm, 407 nm, and 337 nm, respectively. Compared with compound 3, the HOMO \rightarrow LUMO transition of 5 (516 nm) is greatly red shifted, as a result of the "push-and-pull" effect arising from the electron-donating dithioles and the electron-withdrawing geminal enediyne groups. The solid thin film of compound 5 gives three absorption bands at 516 nm, 419 nm, and 338 nm, which are similar to those measured in the solution phase. However, it is notable that the HOMO \rightarrow LUMO band (516 nm) of the solid film is significantly enhanced in intensity than that in the solution-phase spectrum. Moreover, a close comparison of the normalized lowenergy bands in the solution-phase and solid-film spectra (inset of Fig. 4) clearly shows a notable redshift of cut-off energy in the solid state. These results can be rationalized by the fact that the molecules of 5 are in a more organized state in the solid film than in solution. TD-DFT calculations show that the $S_0 \rightarrow S_1$ transition of cis 5 is at 541 nm, which is red shifted relative to that of trans 5 (Table S-1, ESI[†]). It is likely that cis 5 has a molecular shape more suitable for solid-state packing than trans 5, and hence becomes more favoured in the solid state.

The frontier molecular orbitals (FMOs) of the most stable conformers of 3 and 5 are depicted in Fig. 5. As can be seen, the HOMO of 3 is mainly populated on the enediyne moieties and the central phenyl ring of the pentacene unit. The LUMO of 3 is evenly distributed along the entire molecular framework. The patterns of the FMOs of compound 5 clearly reveal a donor-acceptor (D–A) characteristic, where the HOMO is distributed along the electron-rich dithioles and central phenyl group, while the LUMO is primarily on the electron-deficient enediyne and central phenyl segments. Compound 5 has a much higher HOMO energy than that of 3, indicating a stronger electron-donating ability due to the presence of dithiole



Fig. 5 Plots and eigenvalues of frontier molecular orbitals (FMOs) for compounds 3 (*cis* conformer) and 5 (*trans* conformer).

groups. The LUMO energy of 5 is slightly higher than that of 3. As such, compound 5 possesses a narrower HOMO–LUMO gap, which is congruous with the results of UV-Vis analysis.

Redox properties of compounds 3 and 5

The redox activity of compounds 3 and 5 was investigated by cyclic voltammetric (CV) and differential pulse voltammetric (DPV) analyses. Fig. 6A shows the CV profiles of compound 3 measured in solution. There are two quasi-reversible redox wave pairs appearing at $E_{\rm pc1}$ = -0.76 V, $E_{\rm pa1}$ = -0.65 V, $E_{\rm pc2}$ = -1.06 V and $E_{pa2} = -0.88$ V, respectively. The first redox couple can be assigned to the reduction/oxidation of the keto groups,^{36,41} while the second is associated with the geminal enediyne moieties^{32,33} which are poorer electron-acceptors than the keto groups. The CV profiles of 5 in solution show amphoteric behaviour (Fig. 6B). In the positive potential window, a quasi-reversible wave pair is seen at E_{pa} = +0.86 V and $E_{\rm pc}$ = +0.48 V, which is due to the redox reactions occurring on the electron-donating dithiole units. In the negative potential window, a quasi-reversible couple is observed at $E_{\rm pc}$ = -1.03 V and $E_{pa} = -0.96$ V. These peaks are consistent with the second redox couple in the cyclic voltammogram of 3, hence confirming that they are due to the electron transfers occurring on the electron-withdrawing enediyne moieties.

The solid thin film of 5 was prepared on the surface of a glassy carbon working electrode by a dropcasting method. The thin film was subjected to CV and DPV analyses (Fig. 6C and D). In contrast to the solution-phase CV data, the first cycle of the CV scan on the thin film of 5 shows a dramatically different profile than the ensuing scan cycles. As can be seen in Fig. 6C, the first forward scan clearly shows a major anodic peak at +0.72 V and a number of minor anodic peaks in the range of +0.86 V to +1.29 V. These features are very different from the CV profiles of 5 measured in the solution phase. During the first reverse scan a cathodic peak emerges at +0.57 V, which is higher than that in the solution phase CV. Starting



Fig. 6 (A) Multi-cycle CV scans of compound 3 dissolved in CH_2Cl_2 . (B) Multi-cycle CV scans of compound 5 dissolved in CH_2Cl_2 . (C) Multi-cycle CV scans of the solid thin film of 5 measured in CH_3CN . (D) DPV profiles of the solid thin film of 5 measured in CH_3CN . Experimental conditions: electrolyte: Bu_4NPF_6 (0.1 M); working electrode: glassy carbon; reference electrode: Ag/AgCl; counter electrode: Pt wire; CV scan rate: 100 mV s⁻¹; DPV pulse width: 50 ms, pulse period: 200 ms, pulse amplitude: 50 mV, step: 4 mV.

from the second cycle of CV scans, the voltammograms show less distinctive redox features and bear more resemblance to those measured in the solution phase. Similar results can also be seen in the DPV data (Fig. 6D), where the first DPV scan shows a very different profile than the following scans. The electrochemical analysis on the solid thin film of 5 concurs with the UV-Vis results; that is, compound 5 has an ordered microscopic structure in the solid state, likely due to strong intermolecular π -stacking. During the multi-cycle CV and DPV scans, the intermolecular interactions within the solid thin film were substantially altered by the redox reactions, which in turn re-oriented the molecules into a less ordered state similar to the solution phase. This outcome indicates that the solidstate ordering of 5 can be modulated by external electrochemical inputs, which might be useful for stimuli-responsive materials or devices.

Generation of carbon-rich polymeric materials with 2 and 3

Compounds 2 and 3 were subjected to a Pd-catalyzed crosscoupling reaction in order to form polymer products. Two synthetic routes were executed as shown in Scheme 2. In the first route, tetrabromide 2 was cross-coupled with phenylacetylene 6 under the Sonogashira–Hagihara coupling conditions. In a similar way, compound 3 after desilylation was cross-coupled with diiodoarene 7 (Scheme 2) through Pd/Cu catalysis. Experimentally, the resulting products **P1** and **P2** were



Scheme 2 Preparation of carbon-rich polymeric materials P1-P3 via transition metal-catalyzed reactions.

obtained as shiny dark-coloured solids, which are insoluble in most organic solvents. The low solubility prevents clear identification of the exact molecular structures of **P1** and **P2**; however, the data of IR, UV-Vis, and CV analyses suggest that these polymers contain extended π -frameworks containing C=C, C=O, and arene units. In theory, **P1** and **P2** should have similar molecular backbones. This is supported by their IR spectral data, which bear great resemblance to one another. It is also interesting to note that the microscopic morphology of **P1** exhibits microporous features with pore sizes on the dimension of a few hundred nanometers as revealed by SEM imaging (see Fig. S-1D, ESI†).

Apart from the Pd-catalyzed polymerization reactions, a Rucatalyzed reaction of compound 3 was also performed (Scheme 2). The enediyne moieties are known to undergo cyclization under Ru-catalysis to afford benzannulated products.⁴² Experimentally, the reaction ended up with the formation of a black solid product (P3) with extremely low solubility in common organic solvents (detailed procedures and characterization are given in the ESI[†]). IR analysis shows the absence of an alkynyl vibrational band, indicating the complete consumption of enediyne groups during the Ru-catalyzed reaction (Fig. S-2A, ESI[†]). The UV-Vis absorption spectrum of P3 features a significant absorption tail in the Vis-NIR region, extending to as far as 1100 nm. This property suggests that P3 has a highly π -extended molecular structure, mostly likely a polymeric product rather than a small molecule. Power XRD and SEM analyses reveal a certain degree of ordering of P3 at the microscopic level (see Fig. S-2C and S-3, ESI[†]). Overall, the three reactions described in Scheme 2 demonstrate the potential of compounds 2 and 3 to be used as molecular building blocks in generating carbon-rich polymeric materials. Further studies are warranted in order to fully understand the mechanisms of these reactions as well as the exact molecular structures of the products.

Conclusions

In summary, we have developed synthetic methods for selective functionalization of pentacene-5,7,12,14-tetraone with electron-withdrawing geminal enediyne and electron-donating 1,3-dithiole groups to yield new π -conjugated D/A systems with intriguing electronic and redox properties. The geminal enediyne moieties can provide synthetic access to π -extended carbon-rich materials through transition metal-catalyzed reactions. We anticipate that the pentacenedione derivatives reported in this work offer access to a new family of redoxactive π -building blocks and have application in the preparation of novel π -conjugated carbon nanomaterials.

Experimental section

Chemicals were purchased from commercial suppliers and used directly without purification. All reactions were conducted in standard, dry glassware and under an inert atmosphere of nitrogen (N_2) unless otherwise noted. Evaporation and concentration were carried out with a rotary evaporator. column chromatography was performed Flash with 240-400 mesh silica gel, and thin-layer chromatography (TLC) was carried out with silica gel F254 covered on plastic sheets and visualized by UV light. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 300 MHz multinuclear spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to the signals of the internal reference SiMe₄ or residual solvents (CHCl₃: $\delta_{\rm H}$ = 7.24 ppm, $\delta_{\rm C}$ = 77.2 ppm; CH₂Cl₂: $\delta_{\rm H}$ = 5.32 ppm, $\delta_{\rm C}$ = 54.0 ppm). Coupling constants (*J*) are given in Hz. Infrared spectra (IR) were recorded on a Bruker Alfa spectrometer. High resolution APCI-TOF MS analysis was done on a GCT premier Micromass Technologies instrument. UV-Vis absorption spectra were recorded on a Cary 6000i spectrophotometer. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) analyses were carried out in a standard three-electrode setup controlled by a BASi Epsilon potentiostat. Powder X-ray diffraction (XRD) analysis was performed on a Rigaku Ultima IV diffractometer equipped with a copper X-ray source with a wavelength of 1.54 nm. Scanning electron microscopy (SEM) imaging was performed on an FEI MLA 650 FEG microscope. Compounds 1,⁴³ 4,^{44,45} 6,⁴⁶ 7,⁴⁶ and $RuCl_2(PPh_3)(\eta^6-p-cymene)^{47}$ were prepared according to literature procedures. Molecular modelling studies were carried out using Gaussian 09 software.48 Visualization of the calculated molecular structures and orbitals was performed by using the CYLview⁴⁹ and GaussView 5⁵⁰ software packages.

7,14-Bis(dibromomethylene)pentacene-5,12(7H,14H)-dione (2)

Pentacene-5,7,12,14-tetraone (1) (0.30 g, 0.89 mmol) and PPh₃ (2.3 g, 8.9 mmol) were mixed in $CHCl_3$ (100 mL) under an

atmosphere of N₂. The mixture was stirred for 10 min at room temperature, and then CBr₄ (1.5 g, 4.5 mmol) was added. The resulting mixture was refluxed overnight. The white precipitate was filtered off, and then the filtrate was washed with brine, water, and dried over MgSO₄. The organic layer was collected and concentrated under vacuum. The residue was subjected to silica flash column chromatography (CH₂Cl₂/hexanes, 1:1) to yield compound 2 (0.35 g, 0.45 mmol, 60%) as a white solid. IR (neat) ν_{max} : 3064, 1671, 1582, 1330, 951, 682 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.80 (s, 2H), 8.32 (dd, J = 5.8, 3.3 Hz, 2H), 7.89 (dd, J = 5.8, 3.3 Hz, 2H), 7.82 (dd, J = 5.8, 3.3 Hz, 2H), 7.35 (dd, J = 5.8, 3.3 Hz, 2H), ¹³C NMR (75 MHz, CDCl₃): δ 182.3, 141.2, 138.4, 135.0, 134.4, 133.5, 131.5, 127.9, 127.7, 127.4, 126.9, 93.3. HRMS (APCI, positive mode): m/z calcd for [C₂₄H₁₁Br₄O₂]⁺ (M + H⁺): 650.7452; found: 650.7436.

7,14-Bis(1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ylidene) pentacene-5,12(7*H*,14*H*)-dione (3)

Compound 2 (0.25 g, 0.38 mmol) was dissolved in dry Et₃N (15 mL). To this solution were added Pd(PPh₃)₂Cl₂ (27 mg, 0.038 mmol) and CuI (2.3 mg, 0.019 mmol). The mixture was heated to 65 °C. TMSA (0.37 g, 3.8 mmol) was then added dropwise via a syringe over 5 min. The resulting mixture was heated for another 2 h. Et₃N was then removed under vacuum, and the residue was subjected to silica flash column chromatography (CH₂Cl₂/hexanes, 1:9) to yield compound 3 (0.24 g, 0.33 mmol, 87%) as a yellow solid. IR (neat) ν_{max} : 2957, 2898, 2143, 2119, 1680, 1590, 1208, 910, 646 cm⁻¹; ¹H NMR (300 MHz, $CDCl_3$): δ 9.27 (s, 2H), 8.35 (td, J = 5.7, 3.3 Hz, 4H), 7.83 (dd, J = 5.8, 3.3 Hz, 2H), 7.36 (dd, J = 5.9, 3.3 Hz, 2H), 0.28 (s, 18H), 0.26 (s, 18H). ¹³C NMR (75 MHz, $CDCl_3$): δ 182.6, 146.1, 139.6, 134.3, 134.19, 133.7, 131.7, 127.9, 127.9, 127.5, 127.1, 103.5, 103.4, 103.1, 102.6, 102.1, 0.0. HRMS (APCI, positive mode): m/z calcd for $[C_{44}H_{47}O_2Si_4]^+$ (M + H⁺): 719.2653; found: 719.2634.

Compound 5

Compound 3 (0.15 g, 0.21 mmol) and 1,3-dithiole-2-thione 4 (0.22 g, 0.46 mmol) were mixed in P(OEt)₃ (10 mL), and the mixture was heated to 110 °C for 5 h. The unreacted P(OEt)₃ was then removed under reduced pressure. The residue was subjected to silica flash column chromatography (CH₂Cl₂/ hexanes, 1:9) to yield pure compound 5 (0.17 g, 0.11 mmol, 52%) as a dark red semisolid. IR (neat) ν_{max} : 2954, 2923, 2852, 2141, 1531, 1490, 1418, 1248, 932 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂): δ 8.83 (s, 2H), 8.44 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.60 (dd, J = 5.8, 3.3 Hz, 2H), 7.42 (dd, J = 5.9, 3.3 Hz, 2H), 7.37 (dd, J = 5.8, 3.3 Hz, 2H), 2.92-2.73 (m, 8H), 1.83-1.59 (m, 8H), 1.39-1.22 (m, 56H), 0.91 (t, J = 6.6 Hz, 12H), 0.30 (s, 18H), 0.26 (s, 18H). ¹³C NMR (75 MHz, CD_2Cl_2): δ 147.4, 135.8, 134.6, 133.6, 132.4, 128.6, 128.2, 127.8, 127.3, 127.2, 126.3, 124.2, 122.8, 104.1, 103.5, 102.8, 101.8, 101.2, 37.3, 37.1, 32.6, 30.5, 30.44, 30.38, 30.35, 30.32, 30.31, 30.14, 30.13, 30.03, 29.95, 29.92, 29.30, 29.25, 23.8, 14.6, 0.0, -0.1. HRMS (APCI, positive mode) m/z calcd for $[C_{90}H_{131}S_8Si_4]^+$ (M + H⁺): 1580.7127; found: 1580.7113.

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