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Reduced Knoevenagel Reaction of Acetetracenylene-1,2-dione with Acceptor Units for Luminescent Tetracene Derivatives

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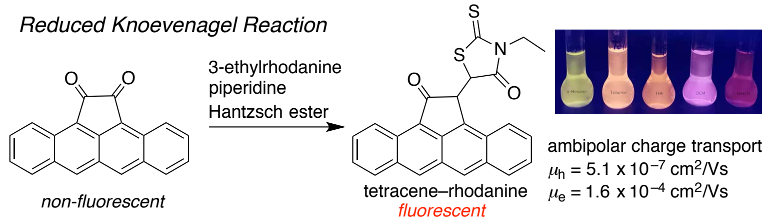


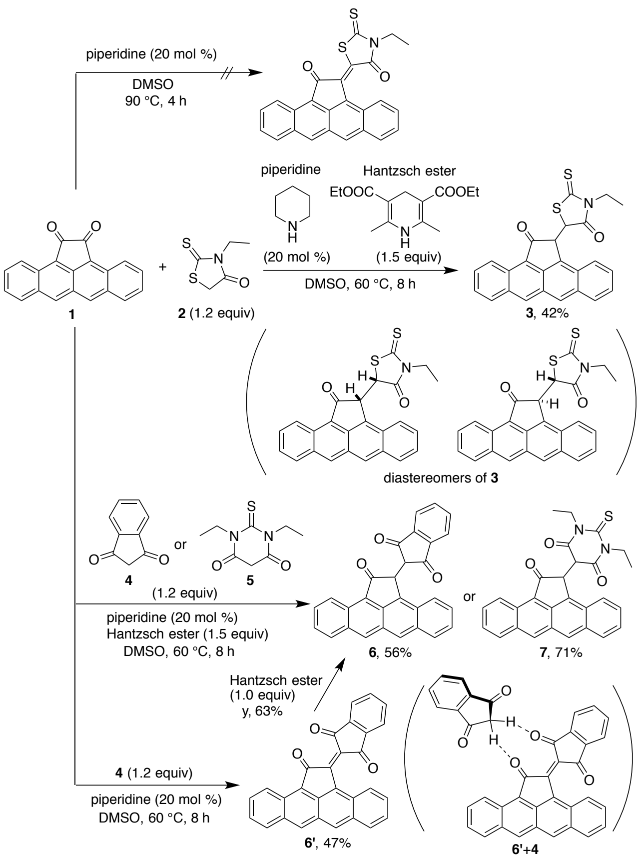
ABSTRACT: Acetetracenylene-1,2-dione reacted with 3-ethylrhodanine in the presence of piperidine and Hantzsch ester via a Knoevenagel condensation–reduction sequence to give a tetracene–rhodanine adduct. This reduced Knoevenagel product exhibited magenta luminescence with fluorescence quantum yield of $\varphi = 0.34$ and fluorescence lifetime of $\tau = 13.2$ ns in toluene. Electrochemical studies and charge carrier transport measurements revealed ambipolar properties with hole and electron mobilities of 5.1×10^{-7} and 1.6×10^{-4} cm^2/(V s), respectively.

Tetracene is a polycyclic aromatic hydrocarbon composed of four linearly fused benzene rings, falling between the size of anthracene (three rings) and pentacene (five rings). Functionalization of tetracene is an intriguing subject because it has greater stability during handling than pentacene and is less well explored than anthracene in terms of derivatization. Modification of tetracene has been investigated for π-system expansion to nano-graphenes[1] and fused π-systems,[2] construction of fused donor–acceptor systems for light harvesting,[3] and other purposes[4]. Expected applications of tetracene derivatives include charge carrier transport materials,[5] organic solar cells,[6] and singlet fission[7]. The luminescence of tetracene derivatives has not been extensively studied,[3a,7a, 8] because the fluorescence quantum yield of tetracene itself is not high ($\varphi = 0.118$ in dichloromethane; $\varphi = 0.17$ in benzene).[3a,7a]

Rhodanine has been widely used in dye chemistry to construct push-pull chromophores.[9] It has recently been used as an electron-withdrawing endcap to construct low-bandgap small-molecule donors[10] and non-fullerene acceptors.[11] Rhodanine also offers easy functionalization because of its active methylene at the 5-position, which acts as a nucleophile and attacks C=O double bonds for constructing π-conjugated structures.

To explore the modification of tetracene, here we aimed to synthesize a linked molecule of tetracene and rhodanine. During this research, an unexpected Knoevenagel condensation–reduction occurred between acetetracenylene-1,2-dione[12] and rhodanine to produce a luminescent tetracene-rhodanine adduct. We also use other nucleophiles to synthesize additional luminescent tetracene derivatives to investigate the scope of the reaction and the functional properties of the derivatives. This study provides useful information on the modification of tetracene for constructing acene-based luminescent functional materials.

Starting from a tetracene diketone, acetetracenylene-1,2-dione (**1**), we first attempted the Knoevenagel condensation with 3-ethylrhodanine (**2**) in the presence of piperidine with the aim of obtaining a conjugated donor (tetracene)–acceptor (rhodanine) adduct (Scheme 1, top). To our surprise, we obtained a reduced product (**3**) instead of the expected Knoevenagel condensation product. Reduced Knoevenagel condensation products have been reported previously,[13] and form via reduction of the Knoevenagel condensation product. Hantzsch ester is often used as an inexpensive commercially available reducing reagent for this reduction reaction. Thus, we used Hantzsch ester to improve the reproducibility of the synthesis. The product could be purified by silica gel column chromatography to separate it from the reaction mixture containing unreacted starting material **1**. Compound **3** was obtained as an air-stable deep-red powder in 42% isolated yield. We consider that the Knoevenagel condensation occurs first, followed by reduction of the intermediate to give the product. The product **3** was much more soluble than pristine tetracene and tetracene diketone **1** in various solvents. This was due to the soluble rhodanine addend and the low crystallinity of the product, which was mixture of two diastereomers with respect to two racemic stereocenters. This improved solubility is beneficial for solution processing to make thin films for use in organic electronics. By using **4** (indane-1,3-dione) and **5** (2-thioxo-dihydro-pyrimidine-4,6-dione) as alternative nucleophiles under the same reaction conditions, we synthesized reduced Knoevenagel condensation products **6** in fair yield and **7** in good yield, respectively. With the advantage of having two carbonyl groups on these addends, **6** and **7** were easier than **3** to separate by silica gel column chromatography, owing to their favorable polarity.



Scheme 1. Reduced Knoevenagel reaction by using piperidine and Hantzsch ester to obtain tetracene derivatives with electron-withdrawing groups.

Product **3** was characterized by ^{1}H and ^{13}C NMR spectroscopy, 2D NMR, and high-resolution ESI-TOF mass spectrometry. The ^{1}H NMR spectrum displayed a signal pattern of a diastereomeric mixture with a major/minor ratio of 4:1 (Figure S2). The spectrum contained 10 proton signals assigned to the asymmetric tetracene moiety and a pair of doublet signals assigned to the methine protons of the reduced part at 5.40 and 5.26 ppm with a coupling constant J = 3.2 Hz in chloroform-*d*. The ^{13}C NMR signals for the reduced part appeared at 51.02 and 53.21 ppm, corresponding to sp^3 methine carbons and confirming the formation of the reduced Knoevenagel product. Thermal stability was confirmed by thermogravimetric analysis, which showed that **3** was stable up to around 250 °C (Figure S14).

Compounds **6** and **7** were also characterized by spectroscopic methods. Both **6** and **7** were easily identified by simple ^{1}H NMR spectroscopy, because these compounds were a racemic mixture of two enantiomers, not a diastereomeric mixture. This merit comes from the use of symmetric active methylene compounds **4** and **5**. Note that, in the ^{1}H NMR spectrum of **7**, the two ethyl groups appeared at different chemical shifts due to restricted rotation around the single bond axis, and two proton signals of the two hydrogen atoms on the α-carbon of the ethyl groups were found to be non-equivalent because of their diastereotopic relationship with the acetetracenylene's methine carbon.

After considerable experimentation, we found that Knoevenagel condensation product **6′** could be isolated as an intermediate in the formation of **6** in the absence of Hantzsch ester. The conjugated product **6′** gradually degraded in solution in air, whereas compound **6** was more stable. We identified **6′** by NMR and high-resolution ESI-TOF MS spectroscopy (Supporting Information). In ^{1}H NMR and ESI mass spectrometry, we observed that **6′** was obtained as a complex with indane-1,3-dione **4** through strong hydrogen bonding between the two acidic (δ+) protons and the two carbonyl groups (Figure S12). We surmise that this intermolecular interaction is vital for the stability of **6′**. By reacting the isolated complex of **6′** and **4** with Hantzsch ester (1.0 equiv) and piperidine (10 mol %) in DMSO for 1 h at 60 °C, we confirmed that **6′** was converted to **6** in 63% yield (Scheme S1).

The UV-vis spectrum of **3** in dichloromethane exhibited a broad absorption spectrum extending up to 600 nm, with absorption maxima at 390, 411, 510, and 540 nm (Figure 1a). This spectral pattern of **3** resembled that of the starting material **1**, indicating the tetracene π-conjugated system was retained during the reaction. Compound **3** exhibited magenta luminescence. Its fluorescence spectrum was broad, ranging from 520 to 800 nm with a maximum at about 580 nm and shoulders at about 625 and 690 nm in dichloromethane (Figure 1b). The absolute fluorescence quantum yield and fluorescence lifetime were φ = 0.23 and τ = 10.4 ns, respectively, in dichloromethane, and φ = 0.34 and τ = 13.2 ns, respectively, in toluene (Table S1). This compound displayed solvato-fluorochromism[14] in which the color changed according to the polarity of the solvent (Figure 1c,d). This phenomenon indicates that intramolecular charge transfer (ICT) contributed to the fluorescence;[15] specifically, the charge-transfer state was stabilized in more polar solvents, thus lowering the energy level of the excited singlet state and causing red-shifted emissions. We consider that this ICT occurs from the tetracene donor to the addend acceptor. Note that the starting material **1** was almost non-luminescent. We surmise that installation of the rhodanine group significantly affected the excited state by changing the charge-transfer properties.

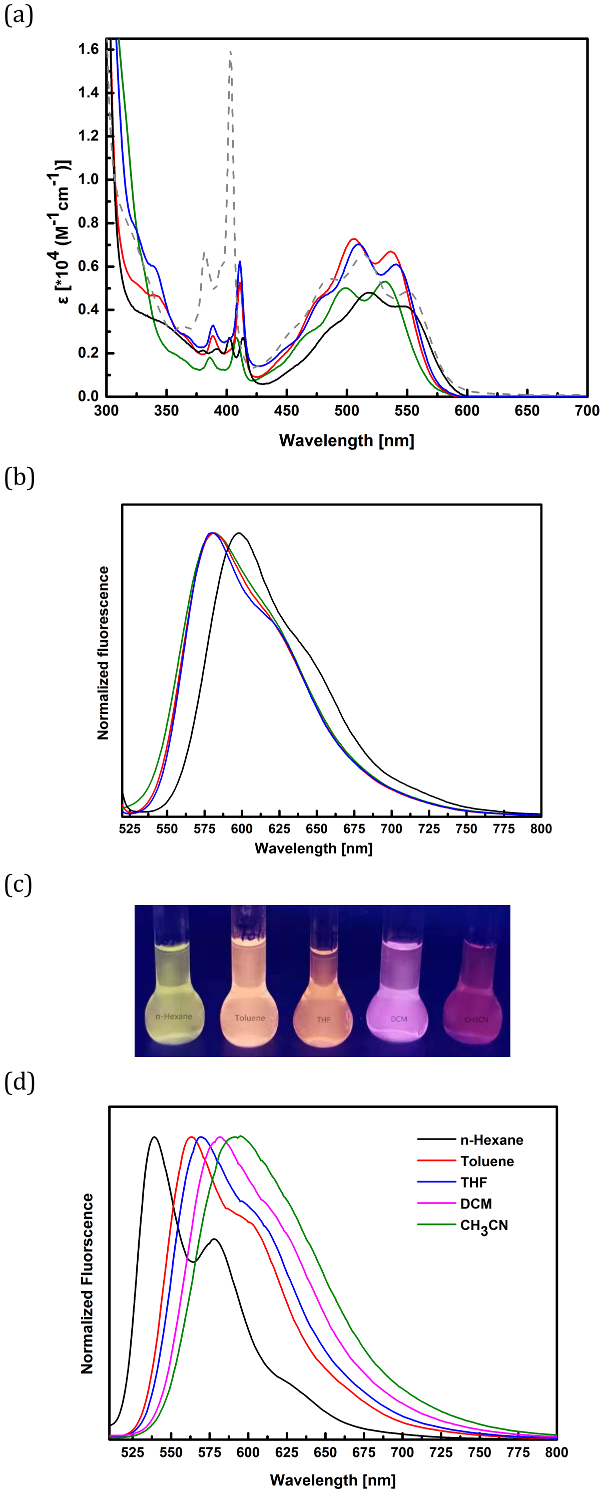


Figure 1. UV-vis and fluorescent spectra of **3**, **6**, **6′**, and **7** (blue, red, black, green lines, respectively) in dichloromethane in room temperature with concentration of 1 x 10^{-5} M. (a) UV-vis absorption spectrum. Absorption maxima in the spectrum for **3** are 380, 411, 510, 540 nm. A gray dashed line denotes an absorption spectrum of **1** in the same condition. (b) Normalized fluorescence spectra (10^{-5} M) at room temperature excited at 510 nm. (c) Solvato-fluorochromism of **3**. From left to right, *n*-hexane, toluene, THF, dichloromethane, and acetonitrile. (d)Normalized fluorescence spectra of **3** in various solvents.

Compounds **6**, **6′**, and **7** showed similar UV-vis absorption and fluorescence spectra (Figure 1a), but **6′** had slightly red-shifted absorption and emission. This red shift was 20–30 nm and was caused by the central double bond in **6′** extending the π-conjugation. The fluorescence quantum yields and fluorescence lifetimes of **6**, **6′**, and **7** were similar to those of **3**: φ = 0.25, 0.19, and 0.24 and τ = 11.0, 8.7, and 10.5 ns for **6**, **6′**, and **7**, respectively, under the same conditions (Table S1).

Next, we investigated the electrochemical properties of **3**, **6**, **6′**, and **7**. Cyclic voltammetry (CV) of the compounds in dichloromethane clearly showed reversible oxidation processes for these compound (Figure S22). However, these compounds exhibited irreversible reduction waves. This is likely because of tautomerization from the diketone form to a diol form with a diene structure, from which a hydrogen atom can be removed in the reduction process to form alkoxide (–O⁻) (Figure S23). However, these reduction potentials appeared as peaks in differential pulse voltammetry (DPV; Figure 2). From these DPV data, we could estimate the frontier orbital energy levels from the equations HOMO = –(4.8 + $E_{1/2}^{\mathrm{ox1}}$) and LUMO = –(4.8 + $E_{1/2}^{\mathrm{red1}}$) eV and the electrochemical bandgap.[16] The HOMO and LUMO energy levels of these compounds were –5.51 to –5.56 eV and –3.26 to –3.33 eV, respectively, suggesting these materials are ambipolar.[6] The electrochemical bandgaps of 2.18 to 2.26 eV were almost identical to those determined from the absorption onset, $E_g = 1240/\lambda_{\mathrm{onset}}$ = 2.10 eV. These bandgaps are smaller than the bandgap of pristine tetracene (2.50 eV).

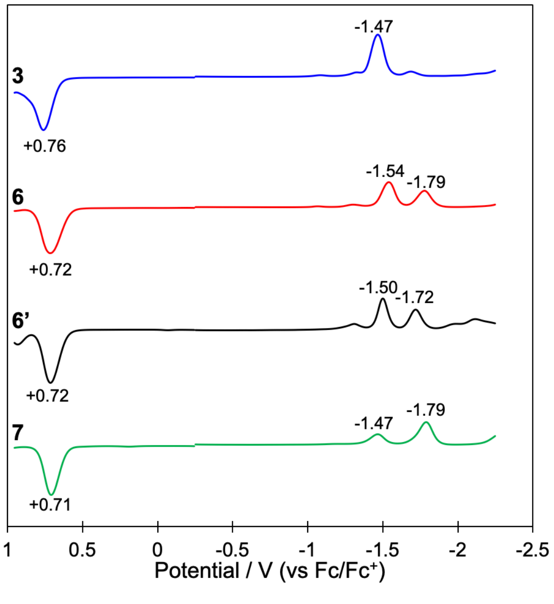


Figure 2. Electrochemical data (DPV) in dichloromethane containing 0.1 M TBAPF$_6$.

To visualize the distribution of frontier molecular orbitals, we performed computational calculations in the Gaussian09 program using density functional theory (DFT) at the B3LYP/6-31G(d) level. First, we optimized the two diastereomeric structures of **3** (Figure 3a-d). Isomer **A** (acetetracenylene-*S*, rhodanine-*S*) was found to be slightly more stable than isomer **B** (acetetracenylene-*R*, rhodanine-*S*), with a small difference in Gibbs free energy of 3.4 kJ/mol. We do not consider here which diastereomer is the major isomer in the reaction. The tetracene plane and the sulfur atom in the five-membered ring of rhodanine are in a staggered conformation in the optimized structures of both **A** and **B**. The calculated HOMO and LUMO distributions of the isomer **A** are shown in Figure 3e,f. Both the HOMO and LUMO are located mainly on the tetracene moiety in conjugation with the carbonyl group. LUMO+1 appears predominantly on the rhodanine unit while LUMO+2 appears partly on it (Figure 3g,h). Thus, we consider ICT could occur from the HOMO to LUMO+1, while the HOMO–LUMO transition is also favorable because of its low transition energy and the similarity of the HOMO and LUMO distributions. The calculated HOMO/LUMO energy levels of **A** and **B** were –5.32/–2.79 and –5.34/–2.81 eV, respectively. Both **A** and **B** had a calculated bandgap of 2.53 eV, which is larger than the values observed from electrochemical and spectroscopic studies. In computations such as this, calculated bandgaps tend to be higher than experimental values.

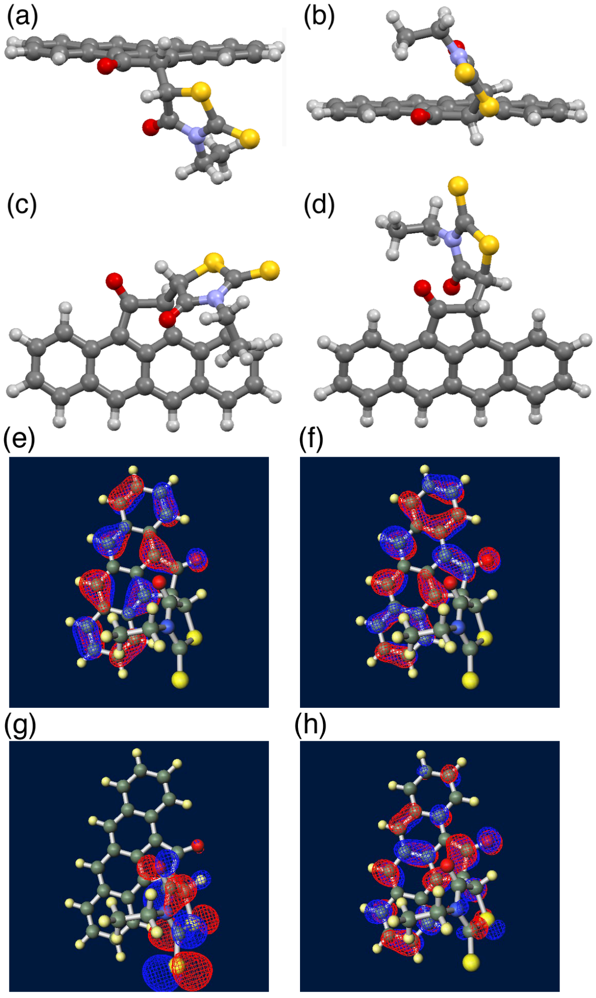


Figure 3. Optimized structures for major and minor isomers of **3** (**A** and **B**) with HOMO and LUMO distribution (B3LYP with a 6-31G(d) basis set). (a) Top view of **A**. (b) Top view of **B**. (c) Side view of **A**. (d) Side view of **B**. (e) Calculated HOMO distribution of computationally more stable isomer **A**. (f) Calculated LUMO distribution of **A**. (g) Calculated LUMO+1 distribution of **A**. (h) Calculated LUMO+2 distribution of **A**.

Computational studies were also performed for **6**, **6′**, and **7** to elucidate their luminescent properties (Figures S24–27). Among the three compounds, only compound **6′** had the LUMO distributed on both the addend and the tetracene unit. The LUMO distribution of **6** and **7** was similar to that of **3**, where the LUMO was located on the tetracene donor and LUMO+1 was located on the addend acceptor.

Space-charge limited current (SCLC)[17] mobility measurements were performed to evaluate the charge carrier mobility of **3**. We fabricated hole-only and electron-only devices with configurations of ITO/PEDOT:PSS/**3**/MoO_3/Al and Al/**3**/Al,[18] respectively (Figures S28 and S29). The high solubility due to this compound being present as a diastereomeric mixture was beneficial for fabricating thin films. Compound **3** was spin-coated from a 20 mg/mL solution in dichloromethane. After annealing at 60 °C for 10 min, good films without pin-holes were obtained (thickness: 60 nm), and hole and electron mobilities were determined to be $\mu_h = 5.1 \times 10^{-7}$ and $\mu_e = 1.6 \times 10^{-4}$ $cm^2/(V\ s)$, respectively. These data suggest that this compound could be useful as an electron transport material in various thin-film organic electronics. We attribute this property mainly to the electron-withdrawing carbonyl moiety attached to the tetracene moiety and to the electron-withdrawing nature of the rhodanine group.

In summary, we demonstrated derivatization of tetracene diketone (acetetracenylene-1,2-dione) by a Knoevenagel condensation–reduction sequence using the nucleophiles 3-ethylrhodanine, indane-1,3-dione, and 2-thioxo-dihydro-pyrimidine-4,6-dione. Product **3** exhibited magenta luminescence with a broad fluorescence spectrum, a fluorescence quantum yield of $\varphi = 0.34$, and a fluorescence lifetime of $\tau = 13.2$ ns (in toluene), and **6** and **7** gave similar luminesce results. Solvato-fluorochromism was observed in which the emission color changed according to solvent polarity, owing to ICT from the tetracene donor to the addend acceptor. The acceptable solubility of these compounds was beneficial for fabricating thin films of good quality. Electrochemical and SCLC measurements revealed ambipolar properties, with hole and electron mobilities of $\mu_h = 5.1 \times 10^{-7}$ and $\mu_e = 1.6 \times 10^{-4}$ $cm^2/(V\ s)$, respectively, for **3**. The better electron mobility than hole mobility suggests that this tetracene compound could be used as a fluorescent n-type material in organic electronics devices. This work will contribute to the design of acene-based functional materials to obtain new organic semiconductors for photoelectronic applications.

Experimental Section

General Information. Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard vacuum-line techniques.

All NMR spectra were taken at 400 MHz (Bruker AVANCE III 400 spectrometer). Unless otherwise specified, all the NMR spectra were recorded in parts per million (ppm, scale) with the proton of tetramethylsilane (TMS) (0.00 ppm) for ^{1}H NMR and carbon of $CDCl_3$ (77.16 ppm) or carbon of DMSO-d_6 (39.52 ppm) for ^{13}C NMR as internal reference, respectively. The data were presented as following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (italic). High-resolution mass spectra (HRMS) were obtained by ESI using a time-of-flight mass analyzer on a Bruker Ultra exTOF/TOF spectrometer. UV-Vis and fluorescent spectra were recorded on a Hitachi U-4100 and Hitachi F-7000 spectrophotometer, equipped with 1 cm quartz cuvette from Starna Cells, Inc. at room temperature. Absolute fluorescent quantum yields and fluorescence lifetimes at room temperature were determined by Quantaurus-QY C11347 (Hamamatsu Photonics) and Quantaurus-Tau C11367 (Hamamatsu Photonics).

Improved Synthetic Procedure for Preparation of the Starting Material 1. To a cold (0 °C) stirred suspension of tetracene (500 mg) in *ortho*-dichlorobenzene (200 mL) was added oxalylchloride (615 mg, 2.2 equiv). To the suspension was then added $AlCl_3$ (anhydrous, powder, 1.17g, 4 equiv) in *ortho*-dichlorobenzene (15 mL) dropwise. (Notice: the $AlCl_3$ was added in three times in 18 h). The suspension was warmed to 25 °C and stirred for another 18 h. The reaction was stopped by addition of 20 mL of MeOH–aqueous HCl (1 M) solution (9:1, v:v). The mixture was concentrated by using an evaporator. The precipitate was added to 300 mL of MeOH–aqueous HCl (1 M) solution (9:1, v:v) and filtered and washed by MeOH to give the crude product (633 mg), which was then sublimated under reduced pressure (0.01 MPa) at 220 °C for 15 h. Consequently, the title compound was obtained as a black solid in 52% yield. The product was confirmed with the spectral data in our previous paper.[12]

General Procedures for the Synthesis of Reduced Knoevenagel products. A dried Schlenk tube with a magnetic stir bar was charged with compound **1** (0.2 mmol), nucleophiles (0.24 mmol, 1.2 equiv), Hantzsch ester (0.3 mmol, 1.5 equiv). The system was evacuated thrice and backfilled with Ar. Next, the solvent DMSO (3.0 mL) and piperidine (20.0 mol %) were added via a syringe. Then, the reaction mixture was stirred at 60 °C for 8 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the reaction was quenched with aqueous HCl (0.1 M) solution (1 mL) and extracted with dichloromethane (10 mL x 3). The organic phase was dried with Na_2SO_4 and the solvent was removed under reduce pressure. The crude mixture was purified by silica gel flash chromatography to give the pure product.

Compound 3. Following the general procedure, 3-ethylrhodanine was used as a nucleophile. The reaction was carried out at 90 °C for 4 h. The product **3** was isolated by flash chromatography (petroleum ether/ethyl acetate = 10/1) as deep red solid in 42% yield (36 mg). Mp 266–270 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 8.7 Hz, 1H), 8.91 (s, 1H), 8.67 (s, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.75–7.67 (m, 1H), 7.58 (dd, *J* = 15.7, 9.2 Hz, 2H), 7.50–7.44 (m, 1H), 5.40 (d, *J* = 3.2 Hz, 1H), 5.26 (d, *J* = 3.2 Hz, 1H), 4.23 (tt, *J* = 7.2, 3.6 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.9, 199.6, 175.3, 141.8, 133.5, 133.4, 133.3, 130.6, 123.0, 129.4, 129.1, 128.9, 127.7, 126.9, 126.6, 126.4, 125.9, 125.9, 125.5, 124.7, 122.8, 53.2, 51.0, 40.3, 11.8. HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{25}H_{18}O_2NS_2$ 428.0774, found 428.0772.

Compound 6. 1H-indane-1,3(2H)-dione (**4**) was used as a nucleophile. The product **6** was isolated by flash chromatography (petroleum ether/ethyl acetate = 10/1) as deep red solid in 56% yield (46 mg). Mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 7.8 Hz, 1H), 8.94 (s, 1H), 8.64 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.04 (dd, *J* = 6.2, 3.6 Hz, 1H), 7.94–7.84 (m, 3H), 7.84–7.74 (m, 2H), 7.72–7.63 (m, 1H), 7.61–7.51 (m, 1H), 7.35 (dd, *J* = 6.4, 3.6 Hz, 2H), 5.19 (d, *J* = 1.7 Hz, 1H), 4.38 (d, *J* = 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.6, 199.0, 197.5, 142.6, 142.2, 141.9, 135.8, 135.5, 133.5, 133.3, 133.2, 131.7, 130.4, 129.5, 129.4, 128.8, 128.4, 126.8, 126.7, 126.4, 126.2, 125.2, 125.0, 124.7, 123.6, 123.4, 123.2, 55.3, 50.0. HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{29}H_{17}O_3$ 413.1172, found 413.1167.

Compound 6′. Hantzsch ester was absence in the synthesis of **6**. The product **6′** was isolated by flash chromatography (petroleum ether/ethyl acetate = 5/1) as deep red solid in 47% yield (51 mg) as **6′**+**4**. Mp 262–263 °C. This compound was obtained as a complex with **4**, which was elucidated by ^{1}H NMR and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.7 Hz, 1H), 8.91 (s, 1H), 8.63 (s, 1H), 8.15 (dd, *J* = 8.5 and 5.8 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.75 (br, 4H, C_6H_4), 7.68 (br, 4H, C_6H_4), 7.64 (t, 1H), 7.54 (t, 1H), 7.34 (t, 1H), 7.26 (t, 1H), 5.34 (s, 2H, CH_2 of indane-dione). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (101 MHz, $CDCl_3$) δ 202.1, 197.2, 197.1, 142.4, 142.4, 135.8, 135.4, 133.7, 133.6, 133.2, 132.0, 130.9, 129.8, 129.5, 129.0, 127.9, 127.5, 126.7, 126.5, 126.4, 125.8, 125.0, 124.9, 124.2, 123.3, 123.2, 60.4. HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{29}H_{15}O_3$ 411.1016, found 411.1017. HRMS (ESI-TOF) *m/z*: [M(**6′**+**4**)+H$^+$] calcd for $C_{38}H_{21}O_5$ 557.1384, found 557.1390.

Compound 7. Following the general procedure, 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**5**) was used as a nucleophile. The product **7** was isolated by flash chromatography (ethyl acetate/MeOH = 20/1) as deep red solid in 74% yield (71 mg). Mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (dd, *J* = 8.7, 0.9 Hz, 1H), 8.95 (s, 1H), 8.67 (s, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.07 (dd, *J* = 5.7, 4.2 Hz, 1H), 7.77–7.69 (m, 2H), 7.63–7.56 (m, 1H), 7.46–7.38 (m, 2H), 5.34 (d, *J* = 1.1 Hz, 1H), 4.86 (d, *J* = 2.1 Hz, 1H), 4.53–4.43 (m, 1H), 4.39 (dd, *J* = 13.1, 7.0 Hz, 1H), 4.27–4.12 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 179.1, 165.9, 164.2, 141.8, 133.4, 133.2, 130.9, 130.6, 129.7, 129.4, 128.9, 127.2, 126.8, 126.6, 126.4, 126.4, 125.2, 124.6, 123.1, 52.5, 51.2, 43.9, 43.4, 12.1, 11.7. HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{28}H_{23}O_3N_2S$ 467.1424, found 467.1420.

Synthesis of compound 6 from the intermediate 6′. A dried Schlenk tube with a magnetic stir bar was charged with compound **6′** (0.02 mmol), Hantzsch ester (5 mg, 1.0 equiv). The system was evacuated thrice and backfilled with Ar. Next, the solvent DMSO (1.0 mL) and piperidine (10 mol %) were added via a syringe. Then, the reaction mixture was stirred at 60 °C for 1 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the reaction was quenched with aqueous HCl (0.1 M) solution (1 mL) and extracted with dichloromethane (10 mL x 3). The organic phase was dried with Na_2SO_4 and the solvent was removed under reduce pressure. The crude mixture was purified by silica gel flash chromatography to give the pure product.

Electrochemical measurements. Cyclic voltammetry and differential pulse voltammetry were performed using CHI660E voltammetric analyzer. All measurements were carried out in a one-compartment cell under argon gas, equipped with a platinum working electrode, a platinum wire counter electrode, and an Ag/Ag^+ reference electrode. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$).

Computational calculation. All calculations were carried out by using Gaussian09 package at the B3LYP. A 6-31G(d) basis set was used for each level. The calculation levels are described as "B3LYP/ 6-31G(d)".

SCLC measurements. The mobility was determined by fitting the dark current to a model of a single-carrier SCLC, which is described by the equation: $J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}$, where J is the current density, μ is the mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, L is the thickness of the tetracene derivative layer, and V is the effective voltage. The thickness of the thin films was measured with a DEKTAK 6M stylus profilometer. A solution of tetracene derivative was spin-coated onto the Al/glass to form a thin film in electron-only devices, and onto the PEDOT:PSS in hole-only devices. The LiF/Al electrodes (LiF = 0.6 nm; Al = 100 nm) or MoO_3/Al were evaporated onto the tetracene derivative thin films in the electron-only devices and hole-only devices, respectively. The experimental dark current density J was measured under an applied voltage swept from –5 to 5 V.

ASSOCIATED CONTENT

Supporting Information

Improved procedures for synthesis of the starting material **1**, ^1H and ^{13}C NMR spectra, and HRMS, thermal stability, fluorescence, computational calculation, SCLC measurements data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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