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PAPER

Linear and star-shaped pyrazine-containing acene dicarboximides with high electron-affinity†

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A series of linear and star-shaped pyrazine-containing acene molecules **1a–b**, **2a–b** and **3** substituted by dicarboximide groups are synthesized *via* condensation reactions between *o*-diamine and dione. High electron affinity (up to 4.01 eV) is achieved due to the introduction of an electron-deficient pyrazine moiety and the attachment of electron-withdrawing dicarboximide groups. Some of these molecules show thermal liquid crystalline behavior and their space-charge limited current mobilities are measured. The high electron affinity and liquid crystalline property qualify them as promising electron transporting materials in organic optoelectronic devices.

Introduction

Organic semiconductors are of great importance and interest from the viewpoint of their fundamental electronic and optoelectronic properties and their potential applications, such as for organic field-effect transistors (OFETs).[1] After large success on hole-transporting (p-type) organic semiconductors,[2] recently there is increasing interest in the development of high performance electron-transporting (n-type) semiconductors, which are desirable for the fabrication of p–n junction diodes, bipolar transistors, and complementary integrated circuits.[3] The general design approaches to achieve n-type semiconductors include (1) attachment of electron-withdrawing substituents (*e.g.* fluorine,[4] carboximide,[5] cyano-[6]) onto the traditional p-type semiconductors (*e.g.* acene, oligothiophene) and/or (2) replacement of the carbon atoms in the framework by electron-deficient atoms (*e.g.* imine nitrogen[7]). Following this guidance, some n-type semiconductors have been successfully synthesized and used in n-channel OFETs.[8]

Linear acene and star-shaped angularly fused acene (*i.e.*, starphene) are good candidates for organic semiconductors and recently electron-deficient n-type acenes[4d,5f,g,6e,7a–f] and starphenes[7m–o,9] have been reported by several groups including us. The substitution by electron-withdrawing dicarboximide groups stabilized the electron-rich acene molecules and also improved their solubility.[5] Replacement of one or more benzene rings in acene and starphene with an electron-deficient pyrazine ring not only increased the electron affinity, but also enhanced intermolecular interactions and improved their kinetic stability towards H_2O and O_2.[7a–e,10] To further increase the electron affinity, herein we are interested in combining both approaches together to design and synthesize new pyrazine-containing acene and starphene dicarboximide derivatives such as the dibenzo-tetraazahexacene[7m,11] bis(dicarboximide)s **1a–b** and **2a–b**, and hexaazatrinaphthylene tris(dicarboximide) **3** (Fig. 1). High electron affinity is expected for these molecules which is a pre-requisite for a good n-type semiconductor. Different alkyl chains are used to tune their solubility and thermal behavior in the solid state.

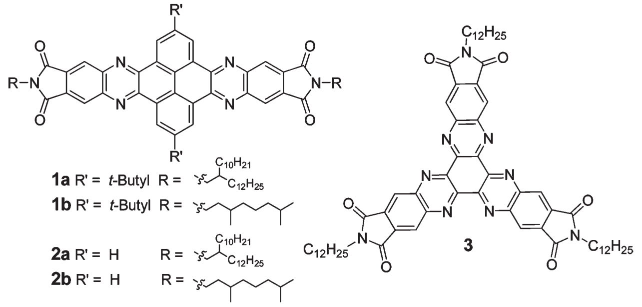

Fig. 1 Chemical structures of nitrogen-rich dibenzohexacene diimides (**1a–b**, **2a–b**) and trinaphthylene trisimide (**3**).

Results and discussion

Synthesis

The synthesis of these electron-deficient compounds is shown in Scheme 1. The formation of pyrazine rings is based on a

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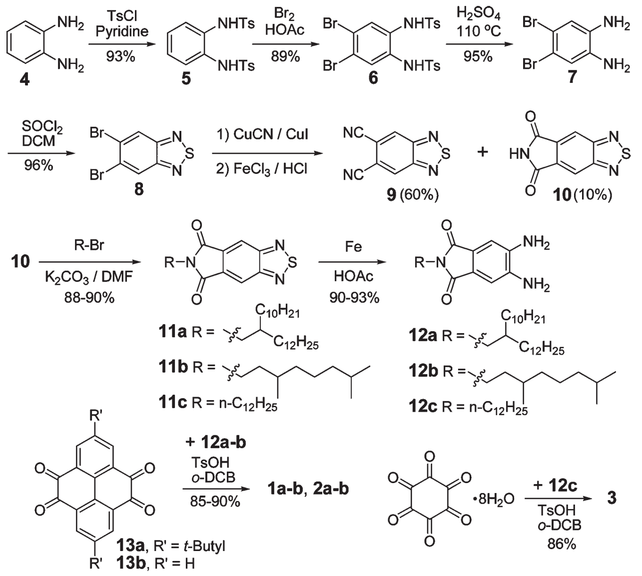
† Electronic supplementary information (ESI) available: Structural characterization data for all new compounds; additional photophysical and electrochemical data; TGA curves; additional DSC curves and POM images; powder XRD data, and additional SCLC data. See DOI: 10.1039/c2ob25680k



Scheme 1 Synthetic scheme for **1a–b**, **2a–b**, and **3**.

condensation reaction between *o*-diamine and dione. The key intermediate compounds are the 1,2-diamino-4,5-phthalimides **12a–c** with different alkyl chains which have never been reported previously. The synthesis started from the protection of *o*-phenylenediamine (**4**) with *p*-toluenesulfonyl chloride (TsCl) in dry pyridine to afford **5** in 93% yield. Bromination of **5** with Br_2 in HOAc gave compound **6** in 89% yield, and subsequent deprotection was conducted by heating **6** in 95% sulfuric acid at 110 °C for about 15 min to give the diamine **7** in 95% yield. Prolongation of the reaction time to 2 h as reported in the literature[12] led to an unknown black solid without **7** at all. The diamine **7** was reacted with $SOCl_2$–Et_3N in DCM to give 5,6-dibromobenzo[*c*][1,2,5]thiadiazole **8** in 96% yield, which was refluxed with CuCN–CuI in nitrobenzene for 6 h, followed by treatment with $FeCl_3$ in HCl solution to give compounds **9** and **10** in 60% and 10% yield, respectively.[13] **9** could be hydrolyzed under acid conditions ($FeCl_3$–HCl) to give **10** in 28% yield. Alkylation of **10** with 1-bromo-3,7-dimethyloctane, 11-(bromomethyl)tricosane,[14] and 1-bromododecane in the presence of K_2CO_3 afforded compounds **11a**, **11b**, and **11c** in 90%, 88%, and 90% yield, respectively.[15] In addition, **11** can also be prepared by treating **9** with the corresponding alkyl amine in *o*-DCB catalyzed by $ZnBr_2$ in around 50% yield. Reduction of **11** was first attempted by using reducing agents such as $NaBH_4$, Zn powder[16] and tin powder, however, all attempts failed to give the desired diamine **12**. Alternatively, a mild reductant, Fe powder, turned out to be an appropriate reductant and the diamines **12a–c** were prepared in 90–93% yields from **11a–c**. Interestingly, all these diamine compounds show good environmental stability in contrast to many other electron-rich diamines.

The linear compounds **1a** and **1b** were then synthesized in 85% and 90% yield, respectively, by a condensation reaction between 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (**13a**)[17] and 2.2 equivalents of **12a–b** in refluxing *o*-DCB in the presence of a catalytic amount of TsOH. Similarly, compounds **2a–b** were prepared under the same conditions from compounds **13b** and **12a–b** in 85% and 90% yield, respectively. The *tert*-butyl group was supposed to facilitate the solubility of **1a–b**,[18] however, to our surprise, **2a** (**2b**) have better solubility than **1a** (**1b**). Condensation between **13a–b** and **12c** gave insoluble materials. The star-shaped hexaaza-trinaphthylene trisimide **3** was prepared in 86% yield by a similar condensation reaction between hexaketocyclohexane octahydrate and 3.3 equivalents of **12c**. Compound **3** showed excellent solubility, such as in DCM, THF, and even in hexane, which allows us to perform various characterizations in solution. ^{1}H NMR, ^{13}C NMR spectroscopy, mass spectrometry (HR-EI MS and MALDI-TOF MS), and elemental analysis were used to identify the chemical structure and purity of all the new compounds (see ESI†).

Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of compounds **1a–b**, **2a–b**, and **3** were recorded in THF solution. It was found that the alkyl chains had almost no effect on the spectra profile (Fig. S1 in ESI†) and thus only the spectra for **1a**, **2a**, and **3** are shown in Fig. 2. All of the three compounds show well-resolved UV-vis absorption and emission bands, with the longest absorption maximum at 431, 429, and 399 nm and the emission maxima at 457, 447, and 504 nm for **1a**, **2a**, and **3**, respectively. The absorption spectra of **1–3** in thin film showed a similar profile to that in solution but with a 12–16 nm red-shift and accompanied with a long tail to the near infrared region, indicating strong intermolecular interactions in the solid state (Fig. S2 in the ESI†).

Electrochemical properties

The electrochemical properties of **1a–b**, **2a–b** and **3** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in DCM solution. As shown in Fig. 3, three quasi-reversible reduction waves were observed for **1a**, **2a**, and **3**, with the onset reduction potential (E_{red}^{onset}) at −1.37, −1.31, and −0.79 V, respectively. Again, the different alkyl chains and *tert*-butyl group have shown little effect on the redox behaviour (Table 1 and Fig. S3 in the ESI†). No obvious redox waves were observed upon oxidation up to 1.8 V. The LUMO energy level

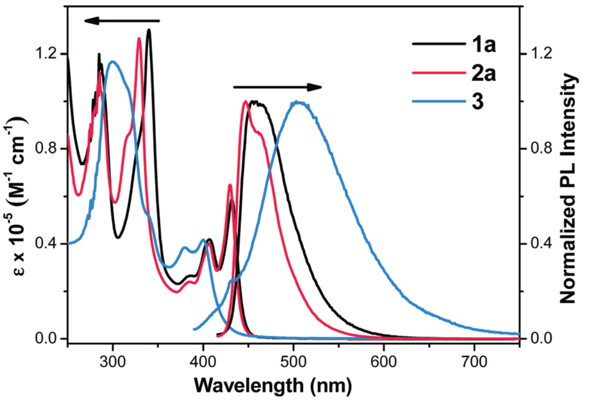


Fig. 2 Absorption and normalized emission spectra of compounds **1a**, **2a**, and **3** in THF.

(electron-affinity) derived from the onset of reduction potential is −3.43, −3.49 and −4.01 eV for **1a**, **2a**, and **3**, respectively.[19] Accordingly, the respective HOMO energy levels are deducted as −6.22, −6.29, and −6.96 eV for **1a**, **2a**, and **3**, respectively, based on the equation HOMO = LUMO − E_g^{opt}, where E_g^{opt} is the optical energy gap determined from the lowest energy absorption onset. Compared with the trinaphthylene tris(dicarboximide)s,[9] after the introduction of six N atoms, the LUMO energy level of **3** was lowered by 0.33 eV from −3.68 eV to −4.01 eV. The electron affinities of **1a–b** and **2a–b** are also increased to *ca.* 0.20 eV compared to their analogs without dicarboximide substituents.[11c] The low-lying LUMO energy level (*i.e.*, large electron affinity) of all compounds indicates that they can serve as promising candidates for n-type devices with good air stability.[8,20]

Thermal behavior and self-assembly in the solid state

The thermal behavior and self-assembly of **1a–b**, **2a–b**, and **3** in the solid state were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). TGA measurements revealed that all compounds were thermally stable over 390 °C with 5% weight loss (see Fig. S4 in the ESI†). DSC curves of **1a**, **1b** and **2b** showed one endothermic transition from the crystalline phase to an isotropic phase (Fig. S5 in ESI†), which was confirmed by POM measurements (Fig. S6 in ESI†). The detailed packing structure at room temperature cannot be simply concluded from their powder XRD patterns (Fig. S7 in ESI†). DSC curves of **2a** exhibited three endothermic transitions at 127, 154 and 167 °C upon heating and three exothermic transitions at 165, 134 and 103 °C upon cooling (Fig. 4). POM measurements disclosed that the compound entered an isotropic phase at around 170 °C. Upon slow cooling, a typical fan-type texture was observed at 160 °C (Fig. 5), indicating an ordered columnar liquid crystalline phase. Upon further cooling below 135 °C, some defects were observed in the fan-type texture, corresponding to the second exothermic transition. Upon further cooling below 103 °C, crystalline domains were observed. The XRD pattern of **2a** recorded at room temperature (Fig. S7 in ESI†) revealed that **2a** has an orthorhombic arrangement with lattice parameter a = 2.68 nm and b = 1.05 nm and γ = 90°.

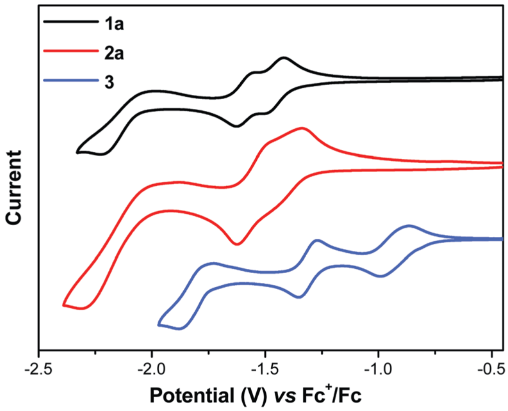


Fig. 3 Cyclic voltammograms of compounds **1a**, **2a**, and **3** in dry DCM with 0.1 M Bu_4NPF_6 as supporting electrolyte, a gold electrode with a diameter of 2 mm, a Pt wire, and an Ag/AgCl electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively, with a scan rate at 100 mV s^{-1}.

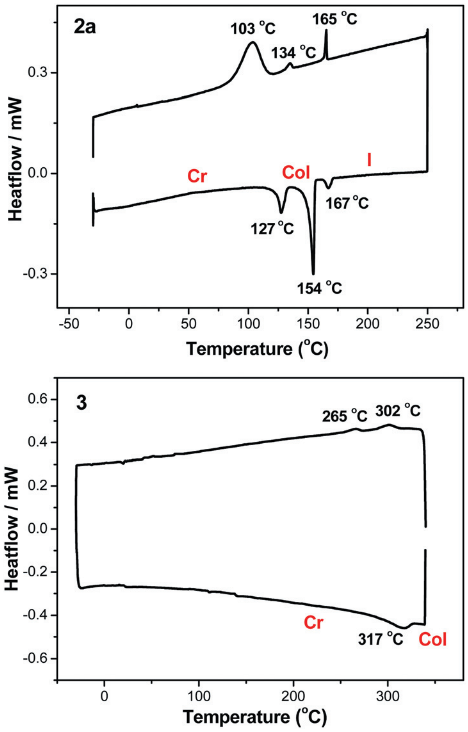


Fig. 4 DSC curves for compounds **2a** and **3** with a heating–cooling scan rate of 10 °C min^{-1} under nitrogen. (Cr = crystalline phase, I = isotropic phase, Col = columnar liquid crystalline phase).

Table 1 Electrochemical data for compounds **1a–b**, **2a–b**, and **3**

	$E_{1/2}^{red(1)}$/V	$E_{1/2}^{red(2)}$/V	$E_{1/2}^{red(3)}$/V	E_{red}^{onset}/V	E_g^a/V	HOMO^b/eV	LUMO^c/eV
1a	−1.43	−1.56	−2.12	−1.37	2.79	−6.22	−3.43
1b	−1.42	−1.57	−2.10	−1.36	2.79	−6.23	−3.44
2a	−1.38	−1.54	−2.15	−1.31	2.80	−6.29	−3.49
2b	−1.39	−1.52	−2.03	−1.30	2.81	−6.31	−3.50
3	−0.91	−1.29	−1.80	−0.79	2.95	−6.96	−4.01

[a] E_g was estimated from the absorption edge in solution. [b] LUMO was calculated according to the equation, LUMO = −(4.80 + E_{red}^{onset}). [c] HOMO was estimated according the equation, HOMO = E_g − LUMO.

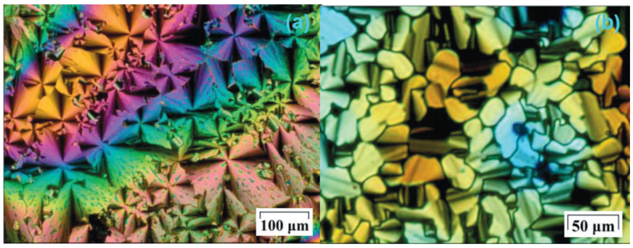


Fig. 5 POM images of (a) **2a** at 160 °C upon cooling and (b) **3** at 345 °C upon heating.

However, the broad reflection peaks in the XRD patterns recorded at 160 °C and 130 °C (Fig. S8 in ESI†) limited detailed analysis of the mesophases. Compound **3** entered into a columnar liquid crystalline phase after 317 °C as demonstrated by the bright focal conic texture recorded at 345 °C upon heating (Fig. 5). XRD pattern of **3** at room temperature showed only one major reflection peak at $2\theta = 2.943°$ and thus the accurate packing structure cannot be figured out.

Space-charge limited-current mobility

Charge carrier mobilities of **1a–b**, **2a–b**, and **3** in thin films were estimated *via* space-charge limited-current (SCLC) technique by using a diode device configuration of ITO–PEDOT : PSS–Al (2 nm)–material–Al. The SCLC is described by $J = 9/8\varepsilon_0\varepsilon_r\mu V^2/d^3$, where ε_0 is the permittivity of free space, ε_r is the relative dielectric constant of the active material estimated from capacitance measurements (assumed to be 3), d is the film thickness, μ is electron mobility, V is the voltage drop across the device, $V = V_{appl} - V_r - V_{bi}$, V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, V_{bi} is the built-in voltage due to the difference in work function of the two electrodes. The resistance of the device was measured using a blank configuration ITO–PEDOT–Al and was found to be about 10–20 Ω. The V_{bi} was determined from the transition between the ohmic region and SCL region and is found to be about 1 V. The film thickness was measured by surface profilometer. The fabricated device was tested in a nitrogen filled glovebox and dark conditions. The current density–voltage (J–V) curves were measured using a Keithley 2400 source measurement unit.

The SCLC electron mobilities were found to be $3–7 \times 10^{-4}$ cm^2 V^{-1} s^{-1} for **1a–b**, **2a–b**, and 3.4×10^{-5} cm^2 V^{-1} s^{-1} for **3** (Fig. 6 and Fig. S9 in ESI†). Unfortunately, our preliminary results show that solution processed thin films of all these compounds only show very weak field effect transistor activity which was also observed for other imine nitrogen-containing semiconductors.[8]

Conclusions

In summary, a series of electron-deficient pyrazine-containing linear and star-shaped acene and starphene molecules end functionalized with dicarboximide groups have been successfully synthesized and their optical properties, electrochemical properties and thermal behavior were investigated. Due to the attachment of electron-withdrawing carboximide groups and the fusion of pyrazine rings, these new compounds showed high electron affinities. Moderate electron mobilities in thin films were also measured *via* the SCLC technique. The observed high electron affinity of these molecules suggests that they can be used as potential electron transporting materials in organic electronic devices.

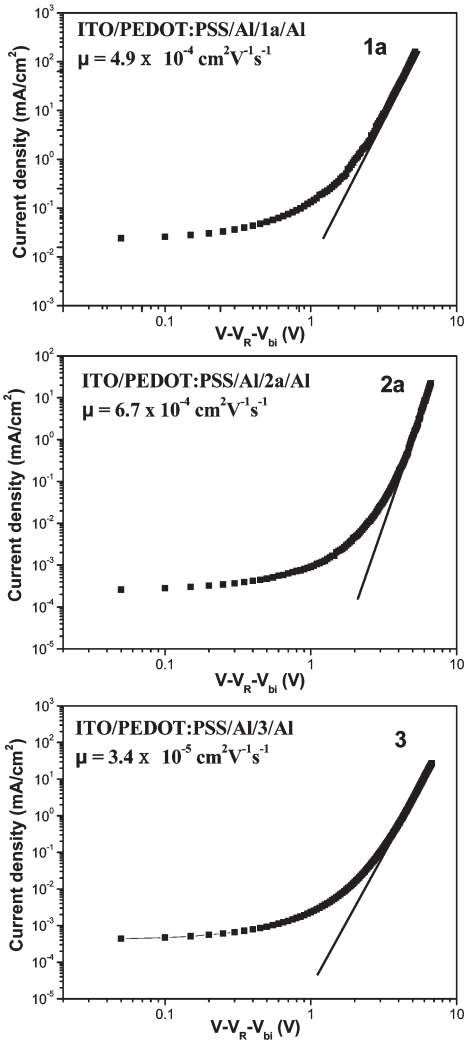


Fig. 6 Double logarithmic plot of the current density (J) *versus* applied voltage (V) curves for **1a**, **2a**, and **3**.

Experimental

General

Anhydrous tetrahydrofuran (THF) and dichloromethane (DCM) were obtained by distillation over sodium and calcium hydride, respectively. 2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone,[17] pyrene-4,5,9,10-tetraone,[17] and 11-(bromomethyl)-tricosane[14] were prepared according to the literature procedures. All other chemicals were purchased from commercial supplies and used without further purification. All NMR spectra were recorded on Bruker AMX500 at 500 MHz and Bruker ACF300 at 300 MHz spectrometers. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. All chemical shifts are quoted in ppm, using the residual solvent peak as a reference standard. Mass spectra were recorded in EI mode and high resolution mass spectra were recorded with EI source. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis was performed on a Bruker Autoflex II MALDI-TOF instrument by using 1,8,9-trihydroxyanthracene as matrix and Pepmix as internal standard or external standard. UV-vis absorption and fluorescence spectra were recorded on Shimadzu UV-1700 and RF-5301 spectrometers in HPLC pure solvents. Cyclic voltammetry was performed on a CHI 620C electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in dry DCM at a scan rate of 100 mV s^{-1}. A gold electrode with a diameter of 2 mm, a Pt wire and an Ag/AgCl electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The potential was calibrated against the ferrocene/ferrocenium couple. Thermogravimetric analysis was carried out on a TA instrument 2960 at a heating rate of 10 °C min^{-1} under N_2 flow, differential scanning calorimetry was performed on a TA instrument 2920 at a heating–cooling rate of 10 °C min^{-1} under N_2 flow. The initial phase transitions and corresponding temperatures for these compounds were determined by an OLYMPUS BX51 polarizing optical microscope equipped with a Linkam TP94 programmable hot stage. VT X-ray diffraction studies were carried out on a Bruker-AXS D8 ADVANCE Powder X-ray diffractometer with Anton Paar Model HTK 1200 High Temperature Chamber and room temperature XRD measurements were performed on a Bruker-AXS D8 DISCOVER with GADDS Powder X-ray diffractometer, both with Cu Kα radiation.

Synthesis and characterizations of 1a–b, 2a–b, and 3

***N,N′*-(1,2-Phenylene)bis(4-methylbenzenesulfonamide) (5).** *o*-Phenylenediamine (540 mmol, 58.5 g) was added slowly to a solution of *p*-toluenesulfonyl chloride (2 eq, 1.080 mol, 205.9 g) in dry pyridine (500 mL) which was cooled to −10 °C in a NaCl–ice bath. The resulting mixture was stirred at room temperature for 18 h. By slow addition of 15% aqueous HCl, a precipitate was formed. The solids were dissolved in EtOH (1400 mL) and refluxed for 1 h, and then stored in a refrigerator overnight for crystallization. After filtration, compound **5** was obtained as a pale solid (210 g, 93%). ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 7.57 (d, J = 8.2 Hz, 4 H), 7.22 (d, J = 8.2 Hz, 4 H), 7.04–7.01 (m, 2 H), 6.98–6.94 (m, 2 H), 6.91 (br, 2 H), 2.39 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 144.15, 135.46, 130.76, 129.60, 127.53, 127.23, 125.96, 21.57. HR-EI-MS (*m*/*z*): calcd for $C_{20}H_{20}N_2O_4S_2$: 416.0864; found 416.0860 (error = −1.0 ppm).

***N,N′*-(4,5-Dibromo-1,2-phenylene)bis(4-methylbenzenesulfonamide) (6).** Bromine (19.2 g, 0.180 mol) was added drop-wise to an ice-cooled and stirred suspension of **5** (37.5 g, 0.090 mol) and anhydrous NaOAc (15.0 g) in glacial acetic acid (150 mL). The mixture was stirred and heated at 110 °C for 3 h, then cooled and poured into ice water (400 mL), and then stirred for an additional 1 h, and EtOH (200 mL) was added. After filtration, the precipitate gave a fine colorless powder of **6** (46 g, 89%). ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 7.60 (d, J = 8.2 Hz, 4 H), 7.28 (d, J = 8.2 Hz, 4 H), 7.20 (s, 2 H), 6.75 (br, 2 H), 2.42 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 144.83, 135.34, 130.89, 130.09, 129.92, 127.64, 122.59, 21.55. HR-EI-MS (*m*/*z*): calcd for $C_{20}H_{18}Br_2N_2O_4S_2$: 571.9075; found 571.9055. (error = −3.5 ppm).

4,5-Dibromobenzene-1,2-diamine (7). The preceding **6** (45.2 g, 78.7 mmol) was heated in concentrated sulphuric acid (90.0 mL) at 110 °C for about 15 min. After cooling to room temperature, the reaction mixture was poured into ice–water and neutralized with 50% NaOH solution until the color of the solution is off-white and lots of precipitate was formed. After filtration, the precipitate gave an off-white powder of **7** (19.3 g, 95%). ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 6.92 (s, 2 H), 3.40 (br, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 135.47, 120.65, 113.62. HR-EI-MS (*m*/*z*): calcd for $C_6H_6Br_2N_2$: 263.8898; found 263.8893 (error = −1.9 ppm).

5,6-Dibromobenzo[*c*][1,2,5]thiadiazole (8). To a solution of **7** (5.32 g, 20.0 mmol) and Et_3N (4.15 eq, 12 mL, 83 mmol) in dry DCM (60 mL) was added, in an ice-cooled condition, a solution of thionyl chloride (2.55 eq, 3.80 mL, 51 mmol) in DCM (10 mL). After addition was complete, the reaction mixture was stirred for 5 h under reflux. After cooling to room temperature, the reaction mixture was filtered, the filtrate was collected while discarding the solid residue, and the solvent was removed under vacuum. The residue was purified with column chromatography using pure DCM as the eluent to give product **8** as a pink–white solid (5.65 g, 96%). ^1H NMR (300 MHz, $CDCl_3$): δ ppm = 8.38 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 153.82, 127.14, 124.90. EI-MS (*m*/*z*): calcd for $C_6H_2Br_2N_2S$: 291.8305; found 291.8305 (error = 0 ppm).

Compound 9 and 10. A mixture of nitrobenzene (40 mL) and dry DMF (120 mL) was added to a stirred mixture of **8** (5.88 g, 20.0 mmol), CuCN (4.1 eq, 82.0 mmol, 7.30 g) and CuI (1.36 g, 7.2 mmol). The mixture was stirred under reflux for 6 h, cooled and poured into a mixture of hydrated $FeCl_3$ (6.8 g), 37% HCl (1.7 mL) and water (10 mL). The suspension was heated at 70 °C for 1 h, and then the solvent removed under vacuum; the residue was dissolved with DCM and water, and extracted with DCM (100 mL). The combined organic phases were washed with HCl (6 M, 200 mL), saturated NaCl (200 mL), and saturated $NaHCO_3$ (200 mL), and was finally dried over Na_2SO_4, concentrated under reduced pressure to give a black residue, which was purified with column chromatography using eluent hexane–EA (5 : 1) to give **9** as a light yellow solid (2.23 g, 60%), and then THF–MeOH (1 : 1) to give **10** as a white solid (0.41 g, 10%).

Compound **9**: ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 8.61 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 153.94, 129.81, 114.65, 113.88. HR-EI-MS (*m*/*z*): calcd for $C_8H_2N_4S$: 186.0000; found 186.0008 (error = 4.3 ppm).

Compound **10**: ^1H NMR (300 MHz, DMSO-d_6): δ ppm = 11.88 (br, 1 H), 8.56 (s, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6): δ ppm = 167.52, 156.16, 132.77, 117.42. HR-EI-MS (*m*/*z*): calcd for $C_8H_3N_3O_2S$: 204.9946; found 204.9939 (error = −3.4 ppm).

General procedure for alkylation of compound 10. A mixture of **10** (8.0 mmol), K_2CO_3 (3.500 g, 24.0 mmol, 3.0 eq), and alkyl bromide (8.4 mmol, 1.05 eq) was heated under argon atmosphere to reflux in DMF (50 mL) for overnight. The reaction was stopped upon complete consumption of the starting material **10** at which point the reaction was cooled and diluted with CH_2Cl_2 (100 mL) and washed with 10% aqueous HCl solution (100 mL × 2) and with saturated aqueous NaCl solution (100 mL × 2), dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using hexane–$CHCl_3$ (4 : 1–10 : 1) as the eluent to give the title compound **11a–c**.

6-(2-Decyltetradecyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7-(6*H*)-dione (11a). 11a: Yield = 83%. Viscous oil. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 8.49 (s, 2 H), 3.67 (d, J = 7.0 Hz, 2 H), 1.94 (br, 1 H), 1.45–1.23 (m, 40 H), 0.89–0.86 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 166.61, 156.66, 131.54, 118.04, 43.07, 40.51, 36.87, 31.85, 31.84, 31.51, 30.92, 29.86, 29.63, 29.61, 29.56, 29.51, 29.29, 26.86, 26.22, 22.61, 14.01. HR-EI-MS (m/z): calcd for $C_{32}H_{51}N_3O_2S$: 541.3702; found 541.3708 (error = 1.1 ppm).

6-(3,7-Dimethyloctyl)-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7-(6*H*)-dione (11b). 11b: Yield = 91%. White solid. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 8.49 (s, 2 H), 3.83–3.76 (m, 2 H), 1.78–1.73 (m, 1 H), 1.54–1.49 (m, 4 H), 1.36–1.13 (m, 5 H), 1.00–0.85 (m, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 166.27, 156.60, 131.62, 117.97, 39.09, 37.11, 36.86, 35.17, 30.73, 27.81, 24.45, 22.56, 22.49, 19.30. HR-EI-MS (m/z): calcd for $C_{18}H_{27}N_3O_2S$: 345.1511; found 345.1513 (error = 0.6 ppm).

6-Dodecyl-5*H*-[1,2,5]thiadiazolo[3,4-*f*]isoindole-5,7(6*H*)-dione (11c). 11c: Yield = 90%. White solid. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 8.50 (s, 2 H), 3.78 (t, J = 7.3 Hz, 2 H), 1.76–1.70 (q, 2 H), 1.35–1.25 (m, 18 H), 0.87 (t, J = 7.0 Hz , 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 166.49, 156.71, 131.66, 118.15, 38.93, 31.87, 29.58, 29.51, 29.43, 29.29, 29.13, 28.33, 26.87, 22.64, 14.06. HR-EI-MS (m/z): calcd for $C_{20}H_{27}N_3O_2S$: 373.1824; found 373.1823 (error = −0.3 ppm).

General procedure for reduction of 11a–c to compound 12a–c. A mixture of **11** (2.0 mmol), iron powder (1.344 g, 24.0 mmol, 12 eq), and glacial acetic acid (20 mL) was heated under reflux for 15–30 min. It was then cooled to room temperature, basified with a solution of NaOH, and extracted with ether. The combined ether extract was washed with a solution of NaOH and water, dried over anhydrous Na_2SO_4, and the solvent was removed to afford a yellow residue which was purified with column chromatography using hexane–THF (1 : 1–3 : 1) to give the final product **12a–c**.

12a: Yield = 92%. Yellow powder. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 7.09 (s, 2 H), 3.83 (br, 4 H), 3.47 (d, J = 7.5 Hz, 2 H), 1.83–1.82 (br, 1 H), 1.33–1.23 (m, 40 H), 0.89–0.86 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 169.51, 139.40, 124.20, 109.98, 41.92, 37.06, 31.81, 31.42, 29.91, 29.59, 29.56, 29.53, 29.52, 29.24, 26.25, 22.57, 13.99. HR-EI-MS (m/z): calcd for $C_{32}H_{55}N_3O_2$: 513.4294; found 513.4273 (error = 4.1 ppm).

12b: Yield = 93%. Yellow powder. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 7.09 (s, 2 H), 3.83 (br, 4 H), 3.62–3.59 (m, 2 H), 1.68–1.61 (m, 1 H), 1.53–1.10 (m, 9 H), 0.94 (d, J = 6.3 Hz, 3 H), 0.84 (d, J = 6.9 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 169.01, 139.29, 124.98, 110.26, 39.24, 37.06, 36.06, 35.70, 30.74, 27.91, 24.55, 22.64, 22.57, 19.40. HR-EI-MS (m/z): calcd for $C_{18}H_{27}N_3O_2$: 317.2103; found 317.2102 (error = 0.3 ppm).

12c. Yield = 93%. Golden yellow powder. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 7.08 (s, 2 H), 3.83 (br, 4 H), 3.57 (t, J = 7.5 Hz, 2 H), 1.63–1.60 (q, 2 H), 1.30–1.24 (m, 18 H), 0.87 (t, J = 7.5 Hz , 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 169.09, 139.30, 124.90, 110.28, 37.79, 31.90, 29.69, 29.60, 29.57, 29.51, 29.32, 29.24, 28.77, 26.89, 22.67, 14.09. HR-EI-MS (m/z): calcd for $C_{20}H_{31}N_3O_2$: 345.2416; found 345.2421 (error = −1.4 ppm).

General procedure for diamine and dione condensation reaction for 1a–b and 2a–b. Diamine **12a–b** (0.22 mmol, 2.2 eq) and 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone or pyrene-4,5,9,10-tetraone (0.1 mmol) were suspended in *o*-DCB (8 mL). A catalytic amount of *p*-toluenesulfonic acid (2 mg) was added. The pH of the solution should be a little acidic at this stage. The resulting solution was stirred and refluxed for overnight under Ar (g) atmosphere. The *o*-DCB was removed under vacuum and the residue was dissolved in DCM and saturated NaCl, extracted with DCM. The combined organic phases were washed with saturated $NaHCO_3$ (200 mL), and then the solvent was removed under reduced pressure to give a yellow residue. The solid residue was purified with column chromatography using hexane–$CHCl_3$ (1 : 1–1 : 5) to give the final product **1a–b** and **2a–b**.

1a: Yield = 81%. Yellow powder. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 9.66 (s, 4 H), 8.55 (s, 4 H), 3.46 (d, J = 5.2 Hz, 4 H), 1.88–1.82 (m, 20 H), 1.24–1.23 (m, 80 H), 0.87–0.84 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 166.88, 151.77, 144.03, 143.90, 130.80, 128.26, 126.33, 126.12, 125.67, 42.83, 36.97, 36.01, 31.91, 31.81, 31.57, 29.97, 29.68, 29.65, 29.59, 29.35, 26.28, 22.67, 14.09. MALDI-TOF MS: m/z = 1329.9659 ($[M + H]^+$); calculated exact mass: 1329.9762. ($[M + H]^+$) Elemental Analysis: calcd for $C_{64}H_{76}N_6O_4$: C, 79.47; H 9.40; N, 6.32; found: C, 79.17; H 9.38; N, 6.30.

1b: Yield = 86%. Yellow powder. ^1H NMR (500 MHz, $CDCl_3$, 323K): δ ppm = 9.83 (s, 4 H), 8.81 (s, 4 H), 3.82 (d, J = 7.5 Hz, 4 H), 1.83–1.54 (m, 20 H), 1.42–1.19 (m, 8 H + 10 H), 1.04 (d, J = 6.3 Hz, 6 H), 0.90 (d, J = 6.9 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, 323K): δ ppm = 166.96, 152.08, 144.51, 144.47, 131.45, 128.82, 126.69, 126.53, 125.97, 39.36, 37.20, 37.13, 36.07, 35.53, 31.79, 31.10, 28.00, 24.64, 22.65, 22.59, 19.49. MALDI-TOF MS: m/z = 937.5888 ($[M + H]^+$); calculated exact mass: 937.5380. ($[M + H]^+$) Elemental Analysis: calcd for $C_{64}H_{76}N_6O_4$: C, 76.89; H, 7.31; N, 8.97; found: C, 76.90; H, 7.29; N, 9.00.

2a: Yield = 88%. Yellow powder. ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 8.39 (d, J = 7.0 Hz, 4 H), 7.71(s, 4 H), 7.36 (t, J = 7.0 Hz, 2H), 3.52 (d, J = 5.1 Hz, 4 H), 1.90 (br, 2 H), 1.40–1.26 (m, 80 H), 0.89–0.86 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 166.35, 143.08, 141.45, 130.75, 128.01, 127.52, 127.07, 125.84, 124.56, 42.89, 37.08, 31.96, 31.94, 31.89, 31.49, 30.12, 29.77, 29.72, 29.66, 29.63, 29.42, 29.39, 29.33, 26.28, 22.70, 22.68, 14.09. MALDI-TOF MS: *m*/*z* = 1217.7934 ($[M + H]^+$); calculated exact mass: 1217.8510. ($[M + H]^+$) Elemental Analysis: calcd for $C_{64}H_{76}N_6O_4$: C, 78.90; H, 8.94; N, 6.90; found: C, 78.75; H, 8.93; N, 6.92.

2b: Yield = 87%. Yellow powder.^{1}H NMR (500 MHz, $CDCl_3$, 323 K): δ ppm = 8.48 (d, *J* = 7.5 Hz, 4 H), 7.77 (s, 4 H), 7.44 (t, *J* = 7.0 Hz, 2 H), 3.67 (t, *J* = 7.5 Hz, 4 H), 1.79–1.20 (m, 2 H + 18 H), 1.40 (d, *J* = 6.3 Hz, 6 H), 0.93 (d, *J* = 6.9 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, 323K): δ ppm = 166.09, 143.28, 141.73, 131.06, 128.21, 127.70, 127.33, 126.16, 124.63, 39.39, 37.13, 35.42, 31.18, 28.03, 24.68, 22.71, 22.64, 19.44. MALDI-TOF MS: *m*/*z* = 825.4212 ($[M + H]^+$); calculated exact mass: 825.4128 ($[M + H]^+$). Elemental Analysis: calcd for $C_{64}H_{76}N_6O_4$: C, 75.70; H, 6.35; N, 10.19; found: C, 75.57; H, 6.34; N, 10.17.

Synthesis of compound 3. Diamine **12c** (0.33 mmol, 114 mg, 3.3 eq) and hexaketocyclohexane octahydrate (0.1 mmol, 31 mg) were suspended in *o*-DCB (8 mL). A catalytic amount of *p*-toluenesulfonic acid (2 mg) was added. The pH of the solution should be a little acidic at this stage. The resulting solution was stirred and refluxed overnight under Ar (g) atmosphere. The *o*-DCB was removed under vacuum and the residue was dissolved in DCM and saturated NaCl, extracted with DCM. The combined organic phases were washed with saturated $NaHCO_3$ (50 mL), and then the solvent was removed under reduced pressure to give yellow residue, which was purified with column chromatography using hexane–THF (1 : 3–1 : 1) to give the final product **3** as a yellow green solid in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm = 9.12 (s, 6 H), 3.86 (t, *J* = 7.5 Hz, 6 H), 1.83–1.77 (m, 6 H), 1.46–1.26 (m, 54 H), 0.87 (t, *J* = 7.0 Hz, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 165.84, 145.76, 143.97, 133.77, 126.53, 39.15, 31.87, 29.60, 29.58, 29.56, 29.47, 29.30, 29.16, 28.40, 26.96, 22.63, 14.05. MALDI-TOF MS: *m*/*z* = 1096.7280 ($[M + H]^+$); calculated exact mass: 1096.6388. ($[M + H]^+$. Elemental Analysis: calcd for $C_{64}H_{76}N_6O_4$: C, 72.30; H, 7.45; N, 11.50; found: C, 72.51; H, 7.44; N, 11.53.

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