Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Organic &
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ARTICLE

Imides Modified Benzopicenes: Synthesis, Solid Structure and Optoelectronic Properties

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Imide-modified polycyclic aromatic hydrocarbons can be widely applied in the field of optoelectronic materials. In this work, we have synthesized four novel functionalized benzopicenes and characterized their solid structures and optoelectronic properties. The fluorescence of the four functionalized benzopicenes showed red shifts with increasing solvent polarity, the quantum yields are high in the solution state and moderate in the solid state. The single crystal structures showed that the benzopicenes adopt a lamellar motif π-stacking. Their good solubility and optoelectronic properties make them potential solution-processable candidates for organic devices, bioimaging and biolabeling.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely found in the combustion residues of coal, wood and other organic materials, and have even been observed in interstellar space.[1] Although some are carcinogenic,[2] PAHs have attracted a great deal of attention owing to their potential applications in organic optoelectronic materials[3] such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVCs).[4] As a classical series of polycyclic aromatic hydrocarbons, acenes and linearly-fused aromatic hydrocarbons have been the subjects of extensive research since Eric Clar first introduced the word acene in 1939.[5] The structure of acenes is considered to be linearly extended one-dimensional graphene and their chemistry has attracted wide interest in both materials[6] and theoretical chemistry.[7] Nonacene is the longest acene reported to date.[8] The most widely studied acene is pentacene (**I**, Scheme 1), which consists of five linearly-fused rings. It has attracted significant attention for use as an organic semiconductor.[9] However, its low solubility and chemical instability hinder device performance. Stability problems can arise from reactions with $^1O_2$ (6,13-endoperoxide formation), but this can be overcome through the introduction of substituents, particularly at the 6,13-positions.[10] Electron-withdrawing substituents decrease the LUMO energy level, which improves the efficiency of n-type semiconductors. For example the introduction of an imide group not only lowers the LUMO but also improves the solubility due to the alkyl groups on the imide unit of PAHs.[11] The aromatic hydrocarbon picene (**II**, Scheme 1) consists of five fused rings and contains a delocalized π-system. Okamoto and co-workers reported the first FET device with thin films of picene showing excellent p-channel

enhancement-type FET characteristics with a μ value of 1.1 cm^2 V^{-1} s^{-1} and an on-off ratio of 1.6×10^5 under an O_2 atmosphere.[12]

Benzopicene (**III**, Scheme 1), which contains one more ring than picene, has rarely been studied despite its relatively simple structure, which may due to its relative synthetic inaccessibility.[13] In the 1990s, Harvey and co-workers developed new approaches to synthesize benzopicene and investigated the carcinogenic oxidized metabolites of benzopicene and its derivatives.[14] Dimethyl-functionalized benzopicene has been synthesized by Krebs and co-workers employing slight changes to Harvey's method and the single crystal structure of dimethylbenzopicene has been discussed in detail.[15] However, to the best of our knowledge, there have been no reports on the optoelectronic properties of benzopicene derivatives, which stimulated us to focus on the synthesis and optoelectronic properties of this unexplored family.

As shown in Scheme 1, benzopicene (**III**) contains two fjord regions, a structural feature expected to cause deviation from planarity.[16] The planarity of PAHs is often deemed to be their most important geometric characteristic;[17] however nonplanar PAHs, which represent a fascinating class of molecules, have received significant attention from organic chemists.[18] Nonplanar PAHs may force aromatic rings to adopt unusual intermolecular interactions because the π surfaces of contorted molecules can induce unusual π-π stacking motifs in self-assembled systems that would be inaccessible with planar species,[19] and can potentially form "self-healing" electronic materials.[20] On the other hand, the introduction of an imide group can lower the LUMO level and improve the solubility due to the alkyl groups on the imide unit, as mentioned previously. Herein we report on the synthesis of novel derivatives of benzopicene with imide groups and their potential applications in optoelectronic materials are discussed.
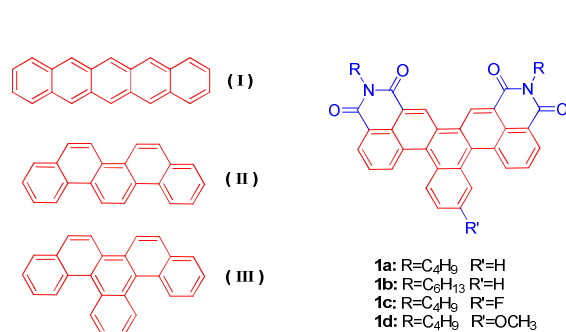
Scheme 1. Structures of pentacene, picene, benzopicene and benzopicenediimide.
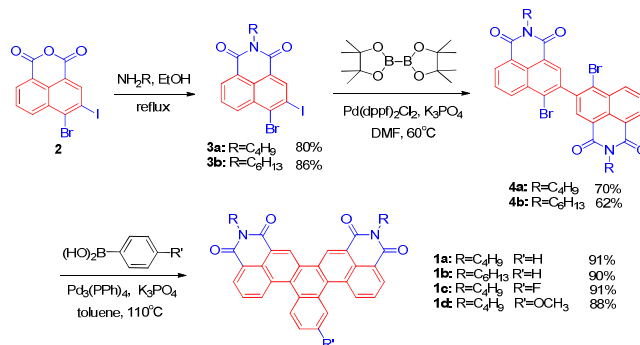
Scheme 2. Synthesis of Compounds **1a-d**.
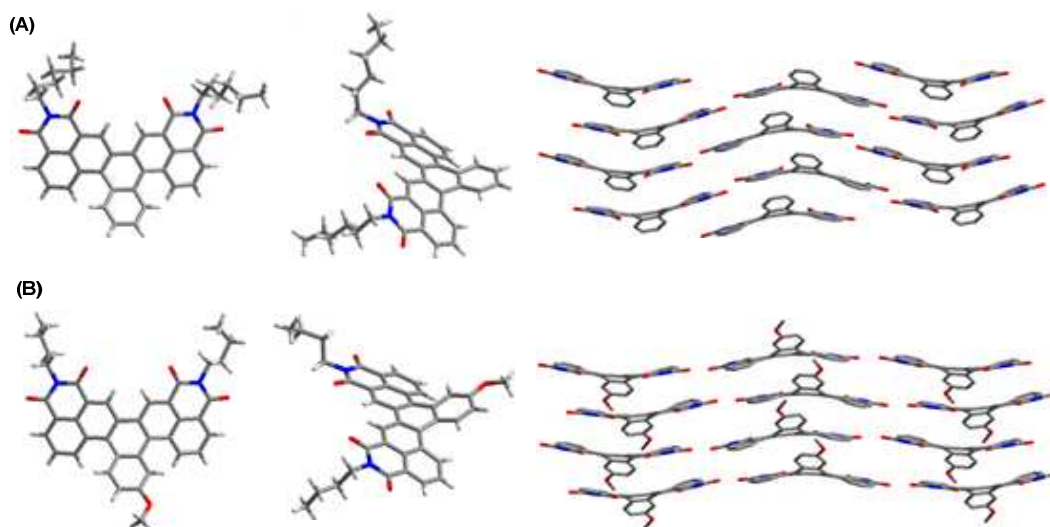
Figure 1. Single crystal structures and packing views of **1b** (A), **1d** (B). Top view, overall view and packing view from left to right. Hydrogen atoms and alkyl-chains have been omitted in packing views for clarity.

Results and Discussion

Synthesis.

The general synthesis of **1a–d** is outlined in Scheme 2. Compound **2** was prepared according to the reported procedure using commercially available 4-bromo-1,8-naphthalic anhydride as the starting material.[21] Compounds **3a–b** were prepared using a slight modification to the reported procedure. The key intermediates **4a** and **4b** were synthesized *via* a Pd-catalyzed cross-coupling reaction in 62−70 % yields. Subsequently, a Pd-catalyzed Suzuki–Miyaura coupling reaction accompanied by C–H transformation was performed to give **1a–d** in 89−91 % yields. The chemical structures of all new compounds were clearly supported by standard spectroscopic characterizations such as NMR and mass spectrometry (see Supporting Information).

Crystal Structures.

The structures of **1b** and **1d** were further confirmed by X-ray crystallographic analysis. Single crystals of **1b** and **1d** suitable for crystallographic analysis were grown by slow diffusion of MeOH into a CH_2Cl_2 solution of **1b** or **1d** and these structures are shown in Figure 1. The four functionalized benzopicenes are favorable for intermolecular charge-transport because of their tendency to aggregate by π–π stacking.[22] As shown in Figure 1, the core moieties of **1b** and **1d** were found to be nonplanar as a consequence of the presence of the fjord region. These two molecules can adopt an "double-concave" conformation which makes them ideal hosts for the binding of different guest molecules at each face.[18c] The central ring of both **1b** and **1d** were not coplanar with twist angles of 19.21° and 19.28°, respectively, which indicates that the alkyl chain length and the introduction of the methoxy group exert virtually no influences on the structure of benzopicenediimide. In addition, there are two[4]helicene structures in each of these four functionalized benzopicenes. Helicene has been investigated for over one hundred years due to theoretical interests in the deformation of the π-system, the aromaticity of helical polyaromatic compounds, their enhanced chiroptical helical properties and their activation energy for racemization. This has led to applications in numerous fields including enantioselective catalysis, chiral recognition and self-assembly, nonlinear optics and molecular switches;[23] and our four novel benzopicenes may find potential applications in the above fields due to their dual [4]helicene structures. While this work was in progress, two other types of helical structures bearing imide groups have been independently reported by Durola[24] and Chen.[25]

As shown in the packing view (Figure 1) both **1b** and **1d** were packed in a one dimensional lamellar motif promoted by π···π stacking interactions and weak C−H···O hydrogen bonds. Along the

b axis, both **1b** and **1d** showed "wave-like" construction with an alternate head to tail array (see Figure S1). Both **1b** and **1d** exhibited close offset face-to-face contacts (around 3.5 Å) and upon to 80% π-orbital overlap in the stacking direction, which is very important in determining the optical and electronic properties of a material (see Figures S2 and S3).[26]

Photophysical Properties.

Because of the presence of alkyl chains, these molecules are highly soluble in common solvents. This good solubility permits facile solution processing and thin film formation. The optical properties were investigated using UV−vis absorption and fluorescence spectroscopies in DCM and these data are shown in Figure 2, Figures S4–S10 and Table 1. All benzopicenediimides displayed well-resolved absorption spectra with maxima at 362, 362, 361 and 369 nm with molar extinction coefficients (ε) of 79510, 74775, 65045 and 86879 M^{-1} cm^{-1}, respectively. In comparison with **1a-c**, **1d** exhibits a slight bathochromic shift. It is possible that the introduction of the methoxy group makes **1d** a donor-acceptor structure; such push–pull systems are known to exhibit narrowed HOMO–LUMO gaps and strong dipoles due to intramolecular charge transfer.[27] The optical energy gaps (E_g) of **1a–d** were calculated from the low-energy absorption onset in the absorption spectra in solution, as shown in Table 1. **1a–c** had the same energy gap of 2.82 eV while **1d** had a smaller energy gap 2.69 eV due to the D-A conformation. The use of donor and acceptor motifs is firmly established, as D-A substitution strongly affects the levels of the frontier orbitals and thus can be modified to tune the optical and electronic properties of a material for the design of organic light-emitting, light-absorbing and semiconducting materials.[28]

The luminescence spectra of compounds **1a–d** have been recorded under 365 nm excitation and revealed Stokes shifts of 79, 78, 84 and 115 nm, respectively. The luminescence spectra of **1a–c** are very similar to each other with each consisting of two peaks, while **1d** exhibits a single peak with a pronounced bathochromic shift. The UV−vis absorption and luminescence spectra of thin films have also been measured as shown in Figure 2 and Figures S4-S5. In the thin film state, the absorption edge of **1a–d** broadened and red-shifted relative to when in solution, implying that the chromophores had a strong tendency to aggregate and/or form J-type aggregates in the solid state.[29] The UV−vis absorption and luminescence spectra of **1a–d** in six different solvents were also measured. The fluorescence of **1a–d** exhibits significant solvatochromism, with increasing bathochromic shifts upon increasing the polarity from cyclohexane to DMSO while the UV−vis absorption has no obvious shifts. The color of the fluorescence markedly changed as shown in Figure 2 and Figures S6-9. This pronounced effect is explained by better stabilization of the excited state with increasing solvent polarity.[30] As compared to **1a-c**, only in cyclohexane does the emission spectrum of **1d** become the mirror image of its absorption spectrum. These findings suggest that solvation relaxation of the singlet excited state of 1**d** does not occur in hexane while it does occur in other solvents (see Figure 2 and figure S6-8).[31]
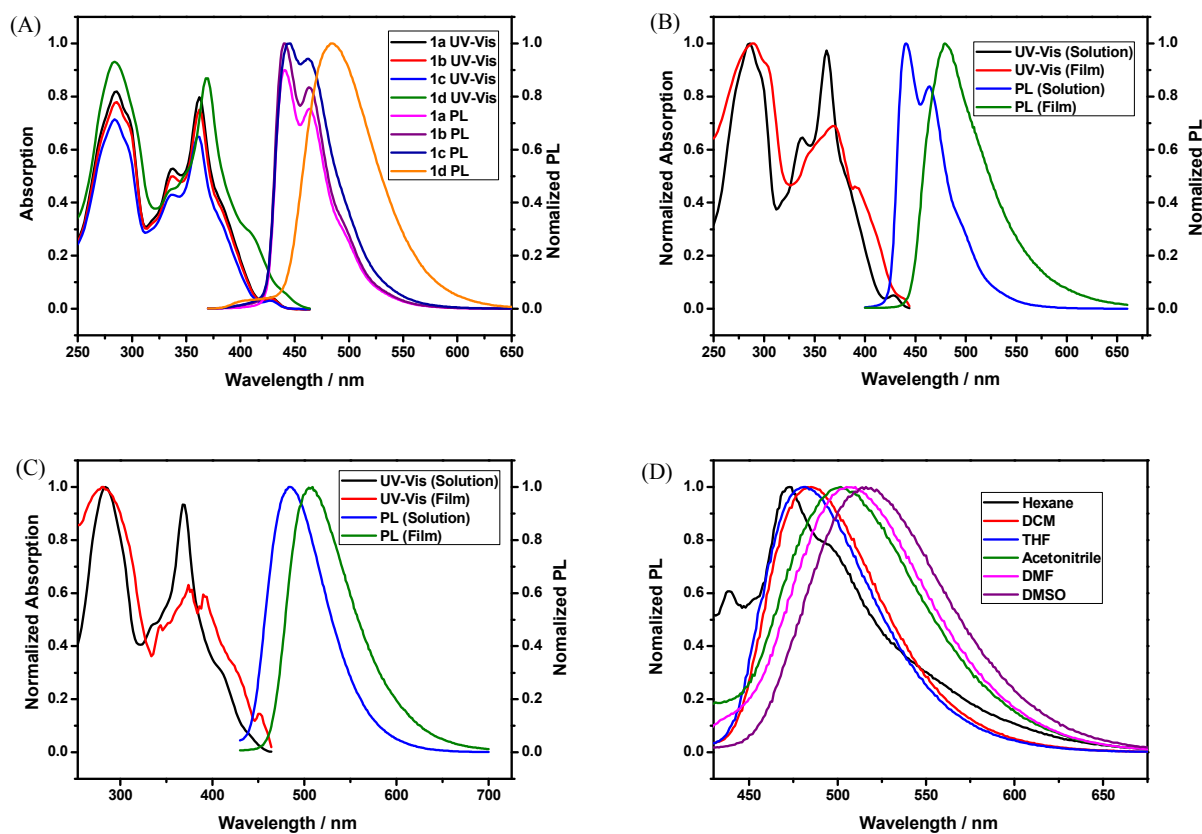

Figure 2. UV−vis absorption and normalized photoluminescence spectra of **1a-d** in DCM (1.0 × 10^{-5} M) (A), normalized UV−vis absorption and photoluminescence spectra of **1a** (B) and **1d** (C) in DCM (1.0 × 10^{-5} M) and in thin film and normalized photoluminescence spectra of **1d** (D) in different solvents (1.0 × 10^{-5} M).

The solvatochromic properties made them potential candidates for sensory applications.[32] The fluorescence quantum yields of **1a-d** were high in the solution state and moderate in the solid state as shown in Figure S8 and table S1, The relative high solid fluorescence quantum yields which may be attributed to the twisted molecular structure and the J-aggregated formation.[33] To the best of our knowledge, the systems of organic dyes with intense fluorescence in both solution and solid state are still limited and these benzopicene derivatives would improve the development of new organic dyes.[25c] The fluorescence lifetime of **1a-d** in dichloromethane and film state were also been measured. In dichloromethane, the fluorescence lifetime of **1a-d** were 9.91, 9.45, 11.33 and 8.49 ns respectively, while those were 6.27, 4.20, 5.42 and 6.60 ns in film state and the Time-resolved luminescence was shown in figure S10.

Electrochemical Properties

The electrochemical properties of **1a–d** were investigated using cyclic voltammetry (CV). The measurements were carried out in dry dichloromethane at room temperature. As shown in Figure 3, **1a**, **1b** and **1d** showed one reversible reduction and one quasi-reversible reduction while **1c** showed two reversible reduction. The two reversible reduction processes of **1c** indicate that the molecules can be reduced into stable anion and dianion which are stabilized by the two imide groups and fluoride atom.[34] The HOMO energy levels of **1a-d** were −6.30, 6.30, 6.27, 6.08 eV, which were estimated based on the onset potential of the oxidation waves. LUMO energy levels of **1a–d**, which were estimated based on the onset potential of the reduction waves, were all below −3.3 eV (Table 1). Frisbie and Gao ever indicated that it could be considered as a potential n-type materials when the LUMO energy level of materials was below −3.0 eV.[35] Accordingly, these imide-modified compounds could well meet the basic requirement of n-type organic semiconductor materials. The energy gaps of **1a–d** were 2.98, 2.98, 2.89 and 2.73 eV, respectively, which were calculated from the CV data. These data are in good agreement with the results calculated from the low-energy absorption onsets, as shown in Table 1.
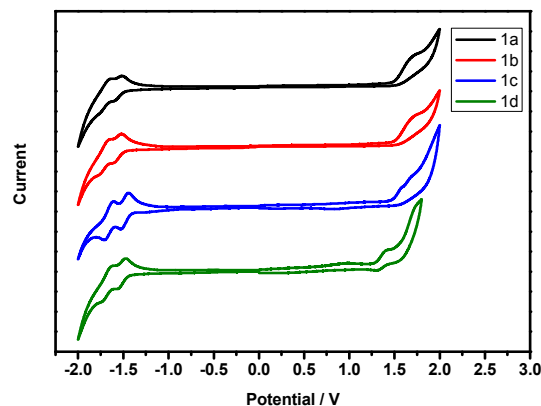

Figure 3. Cyclic voltammogram (CV) of **1a-d** in dry DCM with 0.1 M Bu_4NPF_6 as supporting electrolyte.

DFT Calculations

To gain better insight into the frontier molecular orbitals of **1a−c**, the structures and frontier molecular orbital profiles of these molecules were calculated using DFT calculations at the B3LYP/6-31G* level using the Gaussian 09 suite of programs. Figure 4 the frontier molecular orbital profiles and the optimized structures which show that all four benzopicenediimides exhibit twist conformations despite the slight difference with the crystal structures. As shown in Figure 4, the benzopicene cores possess the largest HOMO and LUMO coefficient and the functional groups had a minor contribution to the frontier molecular orbitals. In addition, although the calculated energy gaps (3.50, 3.49, 3.47 and 3.32 eV) were approximately 0.65 eV higher than the experimental data, the differences between the values for the molecules were negligible, which is in agreement with the experimental data.
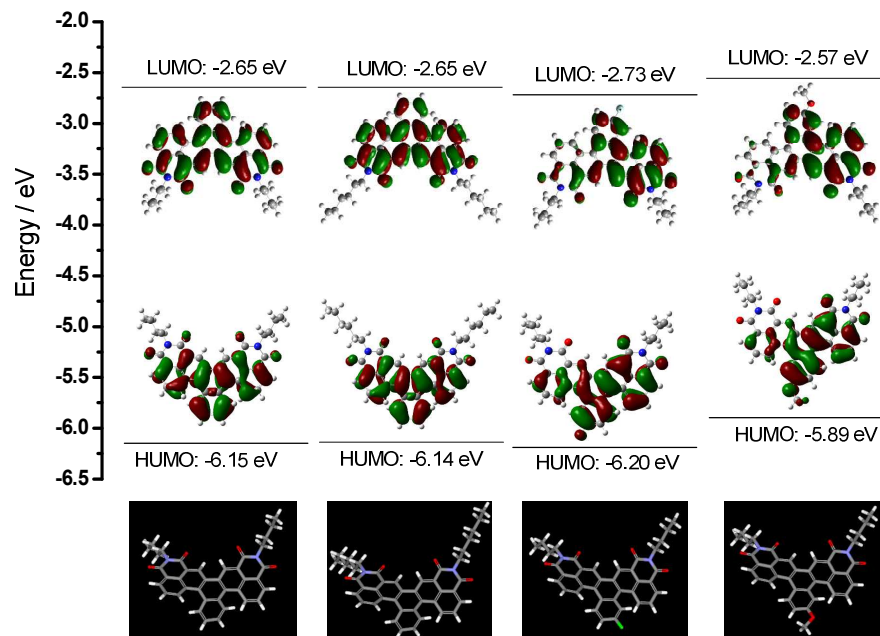

Figure 4. Frontier molecular orbital profiles and optimized structures (bottom) based on DFT (B3LYP/6-31G*) calculations. **1a**, **1b**, **1c** and **1d** from left to right.

Table 1. Optical and Electrochemical Data of Coronenes 1a−d

Compd.	λ_{Abs} [a] [nm]	λ_{max} (PL) [a] [nm]	ε_{max} [b] [$M^{-1}cm^{-1}$]	E_{ox}^{onset} [V]	E_{red}^{onset} [V]	HOMO [c] [eV]	LUMO [d] [eV]	E_g [e] [eV]	E_g [f] [eV]
1a	285, 337, 362 (S [g])	441, 463 (S)	79510	1.50	-1.48	-6.30	-3.32	2.82	3.50
	289, 369, 390 (F [h])	479 (F)							
1b	285, 337, 362 (S)	440, 463 (S)	74775	1.50	-1.48	-6.30	-3.32	2.82	3.49
	290, 371, 390 (F)	479 (F)							
1c	284, 335, 361 (S)	445, 462 (S)	65045	1.47	-1.42	-6.27	-3.38	2.82	3.47
	287, 366 (F)	486 (F)							
1d	285, 335, 369 (S)	484 (S)	86879	1.28	-1.45	-6.08	-3.35	2.69	3.32
	281, 374, 390(F)	508 (F)							

[a] The wavelength of absorption and photoluminescence in CH_2Cl_2 (1.0 ×10^{-5} M); [b] The molar extinction coefficient; [c] HOMO energy levels was calculated from the onset of the first oxidation according to equation: HOMO = -(4.8 + E_{ox}^{onset}) eV; [d] LUMO = -(4.8 + E_{red}^{onset}) eV; [e] E_g was calculated from the low-energy absorption onset in the absorption spectra according to equations: E_g= 1240 / λ_{onset};[36] [f] Obtained from theoretical calculation by DFT. [g] S=Solution, [h] F=Film

Conclusions

In summary, four functionalized benzopicenes were synthesized *via* a facile route in good yields. The molecules exhibit twist conformations and well organized lamellar motif π-stacking, making them promising candidates for supramolecular chemistry. The four benzopicenediimides had good solubility and relatively low LUMO energy levels which render them solution-processable candidates for n-type organic semiconductor applications. Due to their solvatochromic fluorescence, they could potentially serve as sensitive probes in biological systems for the detection of structures, probing dynamics and micropolarity around a biomolecule and interbiomolecular interactions. Studies on their applications for organic devices, bioimaging and biolabeling are currently underway in our laboratories.

Experimental section

General Materials. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. All commercials were used as received without further purification. ^{1}H and ^{13}C NMR spectra were collected on a 400 or 600 MHz spectrometer. UV−vis and fluorescence spectra were obtained on a UV or fluorescent spectrophotometer, respectively. Mass spectra were measured in the EI or MALDI mode. The crystal structure was recorded by X-ray diffraction spectrometer. Elemental analyses were performed by investigation of C, H, N. Cyclic voltammetry (CV) was performed on a potentiostat. A three-electrode one-compartment cell was used to contain the solution of benzopicenediimides and supporting electrolyte in dry CH_2Cl_2. Deaeration of the solution was achieved by bubbling argon through the solution for about 10 min before measurement. A 500 μm diameter platinum disk working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ reference electrode were used. The Ag/Ag$^+$ reference electrode contained an internal solution of 0.01 M AgNO$_3$ in acetonitrile and was incorporated into the cell with a salt bridge containing 0.1 M *n*-Bu$_4$NPF$_6$ in CH_2Cl_2. All electrochemical experiments were carried out

under ambient conditions. The theoretical calculation in the present studies were performed at the B3LYP/6-31G* level by using the Gaussian 09 program.

General Synthetic Procedure for 3a-b. A mixture of 2 (2.01 g, 5 mmol) and *n*-butylamine or *n*-hexylamine (6 mmol) in ethanol (80 mL) was refluxed under argon for 3 h. The resultant solution was evaporated under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane/petroleum ether (1:3, v/v) as eluent to afford pure product as a white solid.

Compound 3b. White solid. Yield: 2.09 g, 86%. Mp = 92–93 °C. ^{1}H NMR(600 MHz, CDCl$_3$): δ_H = 8.93 (s, 1H), 8.61-8.65 (b, 2H), 7.83 (t, J = 7.20 Hz, 1H), 4.15 (t, J = 7.38 Hz, 2H), 1.69-1.70 (b, 2H), 1.53-1.56 (b, 2H), 1.33-1.41 (b, 4H), 0.89 (t, J = 7.02 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 14.0, 22.5, 26.7, 27.9, 31.4, 40.6, 97.6, 121.8, 123.1, 127.9, 128.6, 129.6, 131.2, 140.6, 142.4, 162.1, 163.1. MS (MALDI) m/z: calcd for $C_{18}H_{17}BrINO_2$ 484.949, found 484.561. Anal. Calcd for $C_{18}H_{17}BrINO_2$: C, 44.47; H, 3.52; N, 2.88. Found: C, 44.39; H, 3.61; N, 2.91.

General Synthetic Procedure for 4a−b. A suspension of **3a** or **3b** (1.0 mmol), Pd(dppf)$_2$Cl$_2$ (0.05 mmol), and K$_3$PO$_4$ (3.0 mmol) in DMF (30 mL) was degassed with nitrogen for 15 min at room temperature. Bis(pinacolato)diboron (0.55 mmol) in DMF (20 mL) that was degassed with nitrogen was added to the mixture dropwise with stirring. The mixture was stirred at 60 °C for 4 h, and then the versatile solvents were removed under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane/petroleum ether (3:1, v/v) as eluent to afford pure product as a white solid. The solubility of **4a** and **4b** are not good so that it was hard to get their ^{13}C NMR.

Compound 4a. White solid. Yield: 232 mg, 70%. Mp > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ_H = 8.72-8.76 (m, 4H), 8.55 (s, 2H), 7.96 (t, J = 7.98 Hz, 2H), 4.21 (t, J = 7.32 Hz, 4H), 1.72-1.76 (m, 4H), 1.44-1.48 (m, 4H), 0.99 (t, J = 7.26 Hz, 6H); Anal. Calcd for $C_{32}H_{26}Br_2N_2O_4$: C, 58.03; H, 3.96; N, 4.23. Found: C, 58.10; H, 3.81; N, 4.31. **Compound 4b**. White solid.

Yield: 223 mg, 62%. Mp > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ_H = 8.72-8.76 (m, 4H), 8.55 (s, 2H), 7.96 (t, J = 7.68 Hz, 2H), 4.19 (t, J = 6.78 Hz, 4H), 1.75 (b, 4H), 1.44 (b, 4H), 1.34 (b, 8H), 0.89 (b, 6H); Anal. Calcd for C$_{36}$H$_{64}$Br$_2$N$_2$O$_4$: C, 60.18; H, 4.77; N, 3.90. Found: C, 60.12; H, 4.83; N, 3.83.

General Synthetic Procedure for **1a−d**. **4a** or **4b** (0.1 mmol) was dissolved in toluene (10 mL). After addition of Pd(PPh$_3$)$_4$ (0.005 mmol), K$_3$PO$_4$ (0.3 mmol) and phenylboronic acid (0.11 mmol), the reaction vessel was flushed with nitrogen and stirred at 110 °C for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane/petroleum ether (6:1, v/v) as eluent to afford pure product as a yellow solid.

Compound 1a. Yellow solid. Yield: 53 mg, 91%. Mp > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ_H = 9.36 (s, 2H), 9.11-9.13 (d, J = 8.40 Hz, 2H), 8.73 (b, 2H), 8.63-8.65 (d, J = 7.14 Hz, 2H), 7.90-7.93 (t, J = 7.20 Hz, 2H), 7.84 (b, 2H), 4.17-4.21 (t, J = 7.38 Hz, 4H), 1.72-1.75 (m, 4H), 1.49-1.53 (m, 4H), 1.02-1.05 (t, J = 7.38 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 13.9, 20.4, 30.1, 40.2, 120.8, 122.3, 125.7, 126.1, 126.9, 127.3, 128.6, 129.8, 130.1, 130.3, 131.0, 133.7, 162.9,163.7. MS (EI) m/z: calcd for C$_{38}$H$_{30}$N$_2$O$_4$ 578.22, found 578.47. Anal. Calcd for C$_{38}$H$_{30}$N$_2$O$_4$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.52; H, 5.33; N, 4.91.

Compound 1b. Yellow solid. Yield: 57 mg, 90%. Mp > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ_H = 9.59 (s, 2H), 9.16-9.19 (d, J = 8.40 Hz, 2H), 8.79 (b, 2H), 8.67-8.70 (d, J = 7.16 Hz, 2H), 7.94 (b, 2H), 7.85 (b, 2H), 4.22 (b, 4H), 1.78 (b, 4H), 1.49 (b, 4H), 1.39 (b, 8H), 0.93 (b, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 14.1, 22.6, 26.8, 27.9, 31.6, 40.5, 120.8, 122.3, 125.7, 126.1, 126.9, 127.3, 128.6, 129.8, 130.1, 130.3, 131.0, 133.6, 162.8, 163.6. MS (EI) m/z: calcd for C$_{42}$H$_{38}$N$_2$O$_4$ 634.28, found 634.65. Anal. Calcd for C$_{38}$H$_{30}$N$_2$O$_4$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.51; H, 5.98; N, 4.49.

Compound 1c. Yellow solid. Yield: 54 mg, 91%. Mp > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ_H = 9.75 (s, 1H), 9.74 (s, 1H), 9.17-9.19 (d, J = 8.34 Hz, 1H), 9.11-9.13 (d, J = 8.40 Hz, 1H), 8.82-8.83 (m, 1H), 8.74-8.75 (d, J = 7.14 Hz, 1H), 8.71-8.72 (d, J = 7.20 Hz, 1H), 8.50-8.52 (d, J = 7.80 Hz, 1H), 7.99-8.02 (d, J = 7.80 Hz, 1H), 7.95-7.97 (d, J = 7.80 Hz, 1H), 7.58-7.60 (d, J = 7.20 Hz, 1H), 4.24-4.28 (m, 4H), 1.76-1.81 (m, 4H), 1.51-1.55 (m, 4H), 1.02-1.05 (t, J = 7.20 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 13.7, 20.2, 29.5, 30.1, 40.3, 115.3, 116.8, 117.0, 121.5, 122.2, 122.8, 122.9, 126.2, 126.6, 126.9, 127.2, 127.6, 127.7, 127.8, 130.5, 131.2, 131.9, 132.0, 132.8, 133.4, 160.7, 163.2, 163.7. MS (EI) m/z: calcd for C$_{38}$H$_{29}$N$_2$O$_4$F 596.21, found 596.52. Anal. Calcd for C$_{38}$H$_{29}$N$_2$O$_4$F: C, 76.50; H, 4.90; N, 4.70. Found: C, 76.56; H, 4.97; N, 4.62.

Compound 1d. Yellow solid. Yield: 54 mg, 88%. Mp > 300 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 9.63 (s, 1H), 9.61 (s, 1H), 9.23-9.25 (d, J = 5.48 Hz, 1H), 9.07-9.09 (d, J = 5.56 Hz, 1H), 8.69-8.72 (t, J = 5.60 Hz, 2H), 8.65-8.66 (d, J = 4.60 Hz, 1H), 8.23 (s, 1H), 7.93-7.96 (t, J = 5.20 Hz, 1H), 7.89-7.91 (t, J = 5.48 Hz, 1H), 7.42-7.44 (d, J = 6.28 Hz, 1H), 4.21-4.26 (m, 4H), 4.05 (s, 1H), 1.76-1.79 (m, 4H), 1.51-1.53 (m, 4H), 1.02-1.04 (t, J = 4.88 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 13.8, 20.4,

30.2, 40.4, 55.7, 120.7, 122.8, 123.1, 124.9, 125.9, 126.7, 126.8, 127.1, 127.6, 127.7, 127.9, 128.1, 130.4, 131.0, 132.0, 132.1, 159.6, 163.5, 164.1. MS (EI) m/z: calcd for C$_{39}$H$_{32}$N$_2$O$_5$ 608.23, found 608.54. Anal. Calcd for C$_{39}$H$_{32}$N$_2$O$_5$: C, 76.96; H, 5.30; N, 4.60. Found: C, 76.88; H, 5.37; N, 4.64.

Crystallographic Details. Single crystal of **1b** and **1d** suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of dichloromethane. Crystals with approximate dimensions for **1b** and **1d** were mounted on glass fibers for diffraction experiments. Intensity data were collected on a Nonius Kappa CCD diffractometer with Cu Kα radiation (1.54178 Å) at 298 K. The structure was solved by a combination of direct methods (SHELXS-97)[37] and Fourier difference techniques and refined by fullmatrix least squares (SHELXL-97)[38]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in ideal positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table S2-5.

Computational Details. DFT calculations were performed with the Gaussian 03 and 09 programs, at the B3LYP/3-21G[*] level of theory.

Acknowledgements

Notes and references

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†Electronic Supplementary Information (ESI) available: The ^{1}H NMR, ^{13}C NMR and MS spectra of the new intermediates and Benzopicenediimide. See DOI: 10.1039/b000000x/

1 (a) E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **1953**, *75*, 2667-2672; (b) E. Clar and W. Schmidt, *Tetrahedron*, **1979**, *35*, 2673-2676; (c) R. Scholl, C. Seer and R. Weitzenbk, *Chem. Ber.*, **1910**, *43*, 2202-2209; (d) R. Scholl and C. Seer, *Liebigs Ann. Chem.*, **1912**, *394*, 111-247; (e) R. Scholl and C. Seer, *Chem. Ber.*, **1922**, *55*, 330-341.

2 (a) S. H. Goh and R. G. Harvey, *J. Am. Chem. Soc.*, **1973**, *95*, 242-243; (b) R. G. Harvey, J.-T. Zhang, E. Luna and J. Pataki, *J. Org. Chem.*, **1998**, *63*, 6405-6408.

3 (a) M. D. Watson, A. Fechtenktter and K. Müllen, *Chem. Rev.*, **2001**, *101*, 1267-1300; (b) J. Wu, W. Pisula and K. Müllen, *Chem. Rev.*, **2007**, *107*, 718-747; (c) C. Li, M. Liu, N. G. Pschirer, M. Baumgarten and K. Müllen, *Chem. Rev.*, **2010**, *110*, 6817-6855; (d) T. M. Figueira-Duarte and K. Müllen, *Chem. Rev.*, **2011**, *111*,

7260-7314; (e) J. Mei, Y. Diao, A. L. Appleton, L. Fang and Z. Bao, *J. Am. Chem. Soc.*, **2013**, *135*, 6724-6746.

4   (a) S. Allard, M. Forster, B. Souharce, H. Thiem and U. Scherf, *Angew. Chem. Int. Ed.*, **2008**, *47*, 4070-4098; (b) S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, **2007**, *107*, 1324-1338; (c) W. Pisula, A. K. Mishra, J. Li, M. Baumgarten and K. Müllen, *Org. Photovoltaics*, **2008**, 93-128; (d) B. C. Thompson and J. M. J. Fréchet, *Angew. Chem. Int. Ed.*, **2008**, *47*, 58-77; (e) J. E. Anthony, *Angew. Chem. Int. Ed.*, **2008**, *47*, 452-483; (f) Y. Shirota and H. Kageyama, *Chem. Rev.*, **2007**, *107*, 953-1010; (g) A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay and A. Salleo, *Chem. Rev.*, **2010**, *110*, 3-24; (h) X. Meng, W. Zhu and H. Tian, *Opt. Sci. Eng.*, **2008**, *133*, 129-172; (i) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, **2009**, *109*, 897-1091; (j) M. Mas-Torrent and C. Rovira, *Chem. Soc. Rev.*, **2008**, *37*, 827-838; (k) A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, **2004**, 16, 4556-4573; (l) T. Yamamoto, T. Fukushima, A. Kosaka, W. Jin, Y. Yamamoto, N. Ishii and T. Aida, *Angew. Chem. Int. Ed.*, **2008**, *47*, 1672-1675; (m) Y. Fogel, M. Kastler, Z. Wang, D. Andrienko, G. J. Bodwell and K. Müllen, *J. Am. Chem. Soc.*, **2007**, *129*, 11743-11749; (n) J.-L. Wang, Y. Zhou, Y. Li and J. Pei, *J. Org. Chem.*, **2009**, *74*, 7449-7456; (o) J.-L. Wang, J. Yan, Z.-M, Tang, Q. Xiao, Y. Ma and J. Pei, *J. Am. Chem. Soc.*, **2008**, *130*, 9952-9962; (p) B. Ma, C. H. Woo, Y. Miyamoto and J. M. J. Fréchet, *Chem. Mater.*, **2009**, *21*, 1413-1417; (q) H. Zhang, D. Wu, S. H. Liu and J. Yin, *Curr. Org. Chem.*, **2012**, *16*, 2124-2158.

5   (a) E. Clar, *Chem. Ber.*, **1939**, *72*, 2137-2139; (b) H. Qu and C. Chi, *Curr. Org. Chem.*, **2010**, *14*, 2070-2108.

6   (a) J. E. Anthony, *Chem. Rev.*, **2006**, *106*, 5028–5048; (b) S. Allard, M. Forster, B. Souharce, H. Thiem and U. Scherf, *Angew. Chem. Int. Ed.*, **2008**, *47*, 4070–4098.

7   (a) M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter and F. Wudl, *J. Am. Chem. Soc.*, **2004**, *126*, 7416–7417; (b) D. Jiang and S. Dai, *J. Phys. Chem. A*, **2008**, *112*, 332–335; (c) X. Gao, J. L. Hodgson, D. Jiang, S. B. Zhang, S. Nagase, G. P. Miller and Z. Chen, *Org. Lett.*, **2011**, *13*, 3316–3319; (d) H. F. Bettinger, *Pure. Appl. Chem.*, **2010**, *82*, 905–915.

8   (a) B. Purushothaman, M. Bruzek, S. R. Parkin, A.-F. Miller and J. E. Anthony, *Angew. Chem. Int. Ed.*, **2011**, *50*, 7013–7017; (b) C. Tönshoff and H. F. Bettinger, *Angew. Chem. Int. Ed.*, **2010**, *49*, 4125–4128.

9   (a) M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, **2004**, *104*, 4891–4945; (b) J. E. Anthony, *Chem. Rev.*, **2006**, *106*, 5028–5048; (c) M. Watanabe, K.-Y. Chen, Y. J. Chang and T. J. Chow, *Acc. Chem. Res.*, **2013**, *46*, 1606-1615; (d) M. W. B. Wilson, A. Rao, B. Ehrler and R. H. Friend, *Acc. Chem. Res.*, **2013**, *46*, 1330-1338; (e) M. Mas-Torrent and C. Rovira, *Chem. Soc. Rev.*, **2008**, *37*, 827–838; (f) W. Wu, Y. Liu and D. Zhu, *Chem. Soc. Rev.*, **2010**, *39*, 1489–1502; (g) A. Pron, P. Gawrys, M. Zagorska, D. Djurado and R. Demadrille, *Chem. Soc. Rev.*, **2010**, 39, 2577–2632; (h) H. Klauk, *Chem. Soc. Rev.*, **2010**, 39, 2643–2666; (i) Z. Sun, Q. Ye, C. Chi and J. Wu, *Chem. Soc. Rev.*, **2012**, *41*, 7857–7889; (k) Z. Shuai, H. Geng, W. Xu, Y. Liao and J.-M. André, *Chem. Soc. Rev.*, **2014**, *43*, 2662-2679.

10 W. Fudickar and T. Linker, *J. Am. Chem. Soc.*, **2012**, *134*, 15071–15082.

11 (a) H. Qu, W. Cui, J. Li, J. Shao and C. Chi, *Org. Lett.*, **2011**, *13*, 924–927; (b) S. Katsuta, K. Tanaka, Y. Maruya, S. Mori, S. Masuo, T. Okujima, H. Uno, K. Nakayama and H. Yamada, *Chem.*

Commun., **2011**, *47*, 10112–10114; (c) J. Yin, H. Qu, K. Zhang, J. Luo, X. Zhang, C. Chi and J. Wu, *Org. Lett.*, **2009**, *11*, 3028–3031; (d) J. Yin, K. Zhang, C. Jiao, J. Li, C. Chi and J. Wu, *Tetrahedron Lett.*, **2010**, *51*, 6313-6315; (e) T. Okamoto, T. Suzuki, H. Tanaka, D. Hashizume and Y. Matsuo, *Chem. Asian J.*, **2012**, *7*, 105-111; (f) A. R. Mohebbi, C. Munoz and F. Wudl, *Org. Lett.*, **2011**, *13*, 2560-2563.

12 H. Okamoto, N. Kawasaki, Y. Kaji, Y. Kubozono, A. Fujiwara and M. Yamaji, *J. Am. Chem. Soc.*, **2008**, *130*, 10470–10471.

13 E. Clar, B. A. Mcandrew and J. F. Stephen, *Tetrahedron*, **1970**, *26*, 5465−5478.

14 (a) X-Q. Tang and R. G. Harvey, *J. Org. Chem.*, **1995**, *60*, 3568−3568; (b) R. G. Harvey, J.-T. Zhang, E. Luna and J. Pataki, *J. Org. Chem.*, **1998**, *63*, 6405-6408; (c) F.-J. Zhang, C. Cortez and R. G. Harvey, *J. Org. Chem.*, **2000**, *65*, 3952-3960.

15 F. C. Krebs, M. Jørgensen and M. Larsen, *J. Org. Chem.*, **1999**, *64*, 8758−8760.

16 (a) C. J. Carrell, H. L. Carrell, J. P. Glusker, E. Abu-Shaqara, C. Cortez and R. G. Harvey, *Carcinogenesis*, **1994**, *15*, 2931−2936; (b) S. C. Cheng, A. S. Prakash, M. A. Pigott, B. D. Hilton, H. Lee, R. G. Harvey and A. Dipple, *Carcinogenesis*, **1988**, *9*, 1721−1723; (c) K. Peltonen, S. C. Cheng, B. D. Hilton, H. Lee, C. Cortez, R. G. Harvey and A. Dipple, *J. Org. Chem.*, **1991**, *56*, 4181−4188; (d) J. Szeliga, H. Lee, R. G. Harvey, J. E. Page, H. L. Ross, M. N. Routledge, B. D. Hilton and A. Dipple, *Chem. Res. Toricol.*, **1994**, *7*, 420−427.

17 (a) M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, **2004**, *104*, 4891−4946; (b) H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.*, **2001**, *34*, 359−369; (c) J. Mei, Y. Diao, A. L. Appleton, L. Fang and Z. Bao, *J. Am. Chem. Soc.*, **2013**, *135*, 6724−6746.

18 (a) D. Wu, H. Ge, S. H. Liu and J. Yin, *RSC Adv.*, **2013**, *3*, 22727−22738; (b) D. Pérez, D. Peña and E. Guitián, *Eur. J. Org. Chem.*, **2013**, 5981–6013; (c) Z. Li, N. T. Lucas, Z. Wang and D. Zhu, *J. Org. Chem.*, **2007**, *72*, 3917–3920; (d) Z. Li, L. Zhi, N. T. Lucas and Z. Wang, *Tetrahedron*, **2009**, *65*, 3417–3424; (e) J. Xiao, H. M. Duong, Y. Liu, W. Shi, L. Ji, G. Li, S. Li, X.-W. Liu, J. Ma, F. Wudl and Q. Zhang, *Angew. Chem. Int. Ed.*, **2012**, *51*, 6094–6098; (f) S. Xiao, S. J. Kang, Y. Wu, S. Ahn, J. B. Kim, Y.-L. Loo, T. Siegrist, M. L. Steigerwald, H. Li and C. Nuckolls, *Chem. Sci.*, **2013**, *4*, 2018–2023; (g) S. Xiao, S. J. Kang, Y. Zhong, S. Zhang, A. M. Scott, A. Moscatelli, N. J. Turro, M. L. Steigerwald, H. Li and C. Nuckolls, *Angew. Chem. Int. Ed.*, **2013**, *52*, 4558–4562.

19 (a) Z. Wang, F. Dötz, V. Enkelmann and K. Müllen, *Angew. Chem. Int. Ed.*, **2005**, *44*, 1247–1250; (b) H. Sakurai, T. Daiko, H. Sakane, T. Amaya and T. Hirao, *J. Am. Chem. Soc.*, **2005**, *127*, 11580–11581; (c) C.-Y. Chiu, B. Kim, A. A. Gorodetsky, W. Sattler, S. Wei, A. Sattler, M. Steigerwald and C. Nuckolls, *Chem. Sci.*, **2011**, *2*, 1480–1486; (d) L. Chen, S. R. Puniredd, Y.-Z. Tan, M. Baumgarten, U. Zschieschang, V. Enkelmann, W. Pisula, X. Feng, H. Klauk and K. Müllen, *J. Am. Chem. Soc.*, **2012**, *134*, 17869−17872; (e) L. Chen, K. S. Mali, S. R. Puniredd, M. Baumgarten, K. Parvez, W. Pisula, S. D. Feyter and K. Müllen, *J. Am. Chem. Soc.*, **2013**, *135*, 13531–13537.

20 S. Xiao, M. Myers, Q. Miao, S. Sanaur, K. Pang, M. L. Steigerwald and C. Nuckolls, *Angew. Chem. Int. Ed.*, **2005**, *44*, 7390–7394.

21 (a) X. Meng, W. Zhu, Q. Zhang, Y. Feng, W. Tan and H. Tian, *J. Phys. Chem. B*, **2008**, *112*, 15636–15645; (b) Y. Yang, Y. Xie, Q. Zhang, K. Nakatani, H. Tian and W. Zhu, *Chem. Eur. J.*, **2012**, *18*,

11685–11694.

22 (a) J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei and D. F. Perepichka, *Chem. Mater*., **2008**, *20*, 2484–2494; (b) J. Roncali, P. Leriche and A. Cravino, *Adv. Mate*r., **2007**, *19*, 2045–2060; (c) X. Liu, Y. Wang, J. Gao, L. Jiang, X. Qi, W. Hao, S. Zou, H. Zhang, H. Li and W. Hu, *Chem. Commun*., **2014**, *50*, 442–444; (d) H. T. Black, S. Liu and V. S. Ashby, *Org. Lett.*, **2011**, *13,* 6492–6495.

23 (a) M. Gingras, *Chem. Soc. Rev*., **2013**, *42*, 968–1006; (b) M. Gingras, G. Félix and R. Peresutti, *Chem. Soc. Rev*., **2013**, *42*, 1007–1050; (c) M. Gingras, *Chem. Soc. Rev*., **2013**, *42*, 1051–1095; (d) Y. Shen and C.-F. Chen, *Chem. Rev*., **2012**, *112*, 1463–1535; (e) T. Kogiso, K. Yamamoto, H. Suemune and K. Usui, *Org. Biomol. Chem.*, **2012**, *10*, 2934–2936.

24 H. Bock, D. Subervie, P. Mathey, A. Pradhan, P. Sarkar, P. Dechambenoit, E. A. Hillard and F. Durola, *Org. Lett.*, **2014**, *16*, 1546–1549.

25 (a) Y.-Y. Li, H.-Y. Lu, M. Li, X.-J. Li and C.-F. Chen, *J. Org. Chem.*, **2014**, *79*, 2139–2147; (b) M. Li, L.-H. Feng, H.-Y. Lu, S. Wang and C.-F. Chen, *Adv. Funct. Mater.* **2014**, *24*, 4405–4412. (c) M. Li, Y. Niu, X. Zhu, Q. Peng, H. -Y. Lu, A. Xia, C.-F. Chen, *Chem. Commun.,* 2014, 50, 2993–2995.

26 (a) L. Jiang, H. Dong and W. Hu, *J. Mater. Chem*., **2010**, *20*, 4994–5007; (b) W. Jiang, Y. Li and Z. Wang, *Chem. Soc. Rev*., **2013**, *42*, 6113–6127.

27 L. Zöphel, V. Enkelmann and K. Müllen, *Org. Lett*., **2013**, *15*, 804–807.

28 (a) P. M. Beaujuge, C. M. Amb and J. R. Reynolds, *Acc. Chem. Res*., **2010**, *43*, 1396–1407; (b) Z.-G. Zhang and J. Wang, *J. Mater. Chem*., **2012**, *22*, 4178–4187; (c) C. Li, M. Liu, N. G. Pschirer, M. Baumgarten and K. Müllen, *Chem. Rev*., **2010**, *110*, 6817–6855.

29 (a) E. E. Jelly, *Nature*, **1936**, *138*, 1009–1010; (b) D. Wu, H. Zhang, J. Liang, H. Ge, C. Chi, J. Wu, S. H. Liu and J. Yin, *J. Org. Chem.*, **2012**, *77*, 11319−11324; (c) Y. Hu, Z. L. Wang, X. Yang, Z. Zhao, W. Han, W. Yuan, H. Li, X. Gao and D. Zhu, *Tetrahedron Lett*., **2013**, *54*, 2271–2273.

30 (a) C. Reichardt, *Chem. Rev*., **1994**, *94*, 2319–2358; (b) S. S. Bag, M. K. Pradhan, R. Kundu and S. Jana, *Bioorg. Med. Chem. Lett.*, **2013**, *23*, 96–101; (c) Madhuprasad, N. Swathi, J. R. Manjunatha, U. K. Das, A. N. Shetty and D. R. Trivedi, *New J. Chem.*, **2014**, *38*, 1484-1492; (d) S. Achelle, A. Barsella, C. Baudequin, B. Caro and F. R. Guen, *J. Org. Chem.*, **2012**, *77*, 4087−4096; (e) Y. Zheng, A. S. Batsanov, V. Jankus, F. B. Dias, M. R. Bryce and A. P. Monkman, *J. Org. Chem*., **2011**, *76*, 8300–8310; (f) Y. Dong, A. Bolduc, N. McGregor and W. G. Skene, *Org. Lett*., **2011**, *13*, 1844-1847; (g) M. Hauck, M. Stolte, J. Schönhaber, H.-G. Kuball and T. J. J. Müller, *Chem. Eur. J*., **2011**, *17*, 9984-9998; (h) H.-H. Lin, Y.-C. Chan, J.-W. Chen and C.-C. Chang, *J. Mater. Chem*., **2011**, *21*, 3170–3177; (i) R. Umeda, H. Nishida, M. Otono and Y. Nishiyama, *Tetrahedron Lett*., **2011**, *52*, 5494-5496; (j) A. Fakhari and S. E. Rokita, *Chem. Commun*., **2011**, *47*, 4222–4224; (k) K. Kudo, A. Momotake, Y. Kanna, Y. Nishimura and T. Arai, *Chem. Commun.*, **2011**, *47*, 3867–3869.

31 Y. Ueda, Y. Tanigawa, C. Kitamura, H. Ikeda, Y. Yoshimoto, M. Tanaka, K. Mizuno, H. Kurata and T. Kawase, *Chem. Asian J*., **2013**, *8*, 392–399.

32 G.-F. Zhang, M. P. Aldred, W.-L. Gong, C. Li and M.-Q. Zhu, *Chem. Commun*., **2012**, *48*, 7711–7713.

33 T. E. Kaiser, H. Wang, V. Stepanenko and F. Würthner, *Angew. Chem. Int. Ed*., **2007**, *46*, 5541-5544.

34 J. H. Yao, C. Chi, J. Wu and K.-P. Loh, *Chem. Eur. J*., **2009**, *15*, 9299–9302.

35 (a) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Brédas, P. C. Ewbank and K. R. Mann, *Chem. Mater*., **2004**, *16*, 4436–4451; (b) X. Gao and Y. Hu, *J. Mater. Chem. C*, **2014**, *2*, 3099–3117.

36 C. Chi and G. Wegner, *Macromol. Rapid Commun*., **2005**, *26*, 1532–1537.

37 G. M. Sheldrick, SHELXS-97, a Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, **1997**.

38 G. M. Sheldrick, SHELXL-97, a Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, **1997**.