ChemComm

Chemical Communications

Accepted Manuscript

Volume 54
Number 1
4 January 2018
Pages 1-112

ChemComm

Chemical Communications

rsc.li/chemcomm

COMMUNICATION
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ISSN 1359-7345

ROYAL SOCIETY
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Ambipolar Pentacyclic Diamides with Interesting Electrochemical and Optoelectronic Properties

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Developing organic semiconductors (OSCs) for organic thin film transistors (OTFT) and optoelectronic applications is a challenge. We developed highly crystalline pentacyclic diamides (3) and (4) which showed good OTFT and OLED potential and energy gaps of 2.60 eV and 2.54 eV. They exhibited interesting photo and eletroluminescence activity. Both compounds showed good quantum yields (0.56 for (3) and 0.6 for (4)).

The development of novel and more efficient (opto)electronic devices has become the center of much focus in both chemistry and materials science, due to the profound effect they have on our lives. In this context, there has been an increased focus on novel organic and flexible electronics.[1] In general, organic semiconductors, when compared to traditional Si and GaAs-based technologies, offer unique features such as tunable electronic structure and physicochemical properties via core functionalization, mechanical flexibility as well as variable optical band gaps and ability to be solution processed on a large scale with low cost.[1,2] The introduction of some deformability in the organic semiconductor is a relevant goal that permits for example the fabrication of flexible and printed electronic materials.[1,2] Critical to this goal is the development of more efficient organic semiconductors (OSCs) integrating excellent charge transport with efficient light emission properties.[2] Organic thin film transistors (OTFTs) are particularly important, and the number of publications in this field has exploded since the seminal report by Koezuka in 1987.[3]

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Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

Both the molecular and bulk structures of the OSC are important. In the case of the molecular structure, π-conjugation is an essential prerequisite for a molecule to exhibit such properties. A number of different kinds of molecular systems have been known for some time with this characteristic. These include rubrene, triphenylene, hexabenzocoronene, 5,11-diphenyltetracene (PPT), phthalocyanine, 4,4'-bis(*N*-m-tolyl-*N*-phenylamino)biphenyl (TPD), (PTCDA) – a perylene diimide – and perylenetetra carboxyldiimide (PTCDI),[4] including dioctyl–perylene tetracarboxylic diimide (PTCDI–C_8H_{17})[2a], which is used in n-channel transistors. In the case of bulk structure, supramolecular structure is crucial. The type of crystal packing and intermolecular arrangement is important. Crystalline OSCs show regular and tight packing between neighboring molecules with relatively weak non-covalent bonds, such as hydrogen bonds, van der Waals forces, charge transfer interactions, intermolecular orbital overlap, etc.[4b] The potential of the OSC for OTFT is assessed by determining their charge carrier mobility. Some of the best results were obtained in single crystals. Rubrene was reported by Rogers's group to have an intrinsic hole mobility of 15.4 cm²/Vs.[5] 2,6-di-(2-naphthyl)anthracene, was shown by Hu's group[2] to have a charge carrier mobility value of 12.3 cm²/Vs (including a quantum yield of 29.2% which will be important in the discussion below). 2,7-dioctyl[1]benzothieno[3,2b] benzothiophene (C8-BTBT) was shown by Hasegawa's group to have a value of 16.4 cm²/Vs (saturation regime) attaining a highest value of 31.3 cm²/Vs[6]. Indenone-fused *N*-heteroacenes[7] were shown by Lino's group to give a value of 12.3 cm²/Vs. In the case of imide (and analogue) type OSC the values are less remarkable. Frisbie and coworkers reported a value of 0.1 cm²/Vs (in a thin-film configuration).[8] More recently, Felter's group reported a best value of 0.32 cm²/Vs for the perylene diimide (PDI), known as PDI-octyl (which forms large crystalline aggregates) in a thin-film using pulse radiolysis time-resolved microwave conductivity (TRMC).[9]

Important also is the ambipolar charge transport characteristics of these materials[4b]. In this case, both the electron (μ_e) and hole (μ_h) mobilities are significant. The best compounds usually have a small HOMO-LUMO energy gap.[10] High values for both μ_e and μ_h in the range 3 to 9 cm²/Vs have been reported for a plethora

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of OSCs[4b]. Unfortunately, there are few reports on the determination of these parameters for imide (and analogue) type OSCs. Iyer and coworkers reported a $\mu_e = 0.6$ cm²/Vs for an imide-type OSC (thin films).[11] An amide functionalized coronene, although not a true imide, was shown by De *et al.* to possess high electron and hole mobilities, $\mu_e = 3.59$ cm²/Vs and $\mu_h = 8.84$ cm²/Vs.[10]

In this communication we report on a new family of condensed imide type compounds with interesting OTFT potential and confirmed electroluminescence properties.

For some time, the Burke group has been interested in efficient catalytic routes to certain heterocyclic ring systems.[12] In an attempt to reduce the number of synthetic steps leading to a key dihydroisoquinolinone target (see Scheme s1, supporting information), we inadvertently synthesized the novel chiral fluorescent pentacyclic diamide (**3**) which, in the solid state, exists as a fluorescent crystalline yellow solid (Scheme 1, its crystallinity was confirmed by SEM analysis Fig. s.12(a)). This compound crystallinity was characterized by X-ray crystallography (Fig. s13), which revealed that the compound was slightly twisted, and not completely flat (see Supporting Information for details). Compound (**3**) crystal structure, as shown in Fig. s8, is characterized by several C-H--O bonding interactions which compelled the molecules to form compact layers. A putative mechanism for the synthesis of (**3**) is shown in Scheme s.3 (Supporting Information). Considering the unique structural features of this molecule (significant conjugation, "quasi-flatness" and pseudo-aromaticity) we immediately envisioned this class of molecule should possess potential optoelectronic properties, particularly since phthalimide[10,11] based fluorescent probes are well-known and, thus, embarked on several studies to test this hypothesis. The spectroscopic, cyclic voltammetry and computational analyses are discussed in detail below. We also synthesized via a novel synthetic pathway that involved a crucial McMurry coupling step (Scheme s2 SI) the already reported compound (**4**) (unfortunately this compound was never isolated nor previously characterized)[13], without the methoxyl-substituted group, to compare the results with those of compound (**3**). The more crystalline nature of (**3**) may be due to the presence of stereocenter and the OCH₃ group (see SEM analysis in Fig. s.12). Density-functional theory (DFT) and time-dependent density-functional theory (TD-DFT) calculations were carried out to investigate geometrical, optical and electronic properties of compounds (**3**) and (**4**) (SI).
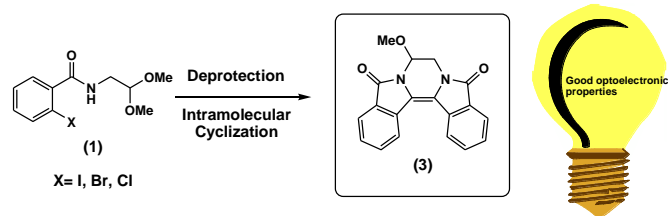
containing the electrolyte tetrabutylammonium perchlorate (TBAP; 0.1 M) under nitrogen flow (Figures 1 and 2 respectively). Compound (**3**) and the unsubstituted parent compound (**4**) both presented one chemically irreversible two electron oxidation wave with an anodic peak potential (E_{pa}) at 1.30 V and 1.27 V respectively. Both compounds also presented two reversible/quasi reversible one-electron transfer reduction waves (E_{pc1}) at −1.45 and -1.52 V and E_{pc2} at -1.73 and -1.83 V (vs SCE), respectively. In the cathodic direct scan, at different scan rates, two successive reversible/quasi-reversible one electron transfer process, with a formal potential of -1.40 V and -1.44 V and -1.69 V and -1.77 V (vs. SCE) were observed, respectively. Semiconductors are usually characterized by having energy gaps (HOMO-LUMO separation) below 3.0 eV. The LUMO energies of (**3**) and (**4**) were estimated to be around -3.29 eV and -3.28 eV, respectively (for comparison, naphthalene bis-imide ambipolar field effect transistors, like TPA-PMPI[14] presented a value of -2.27 eV). The HOMOs have energies of -5.89 eV and -5.82 eV, respectively, determined also from the CV data by using ferrocene as reference to calculate the energy (E_{Homo}= -e[$E_{oxonset}$+4.4]) and LUMO (E_{Lumo}= -e[$E_{redonset}$+4.4]).[15] (The literature determined value for TPA-PMPI[14] was -5.35 eV). The corresponding electrochemical energy gaps (Eg_{EC}) were estimated to be 2.6 eV and 2.54 eV respectively (compared with 3.22 and 3.20 eV calculated by DFT) suggesting indeed that these compounds have semiconductor properties. The agreement of the electrochemical calculated HOMO energies and the DFT calculated values is very good, while for the LUMO energies the difference is ≈ 0.6 eV. It is known that the HOMO values can be estimated by cyclic voltammetry with better accuracy when compared with the LUMO values.[16] It was even suggested the use of electrochemical techniques for determining only the HOMO level and to estimate the LUMO by adding the experimental optical gap value.[17] When we calculate the LUMO energies in this way the agreement with the theoretical calculated values improved remarkably (see Table **1**). In the direct anodic scan, a chemical irreversible two-electron oxidation wave at 1.30 V and 1.27 V suggests that this is an irreversible oxidation process. Coulometry experiments were conducted but it was not possible to isolate any product (see supporting information). These results may indicate limitations for hole transport for amorphous/disordered films.

Scheme 1. Serendipitous synthetic approach to the fluorescent pentacyclic diamide (**3**).

Standard electrochemical properties were studied by cyclic voltammetry (CV) and the spectroelectrochemical UV–Vis-NIR spectra of (**3**) were studied and recorded in acetonitrile (MeCN)

Table 1 The Suite of Electrochemical Parameters Measured for Compounds (**3**) and (**4**). [a] Calculated by adding the optical band gap and CV HOMO level.

Compound	Epc1	E0	Epc2	E0	Epa3	HOMO (eV)		LUMO (eV)		
						CV	DFT	CV	DFT	CV+Opt[a]
(3)	-1.45	-1.40	-1.73	-1.69	1.30	-5.89	-5.95	-3.29	-2.73	-2.87
(4)	-1.52	-1.44	-1.83	-1.77	1.27	-5.82	-5.89	-3.28	-2.68	-2.80

All spectroelectrochemical studies using UV-Vis-NIR spectroscopy of (**3**) and (**4**) were studied and recorded in MeCN with the same electrolyte (TBAP; 0.1 M) under nitrogen flow. As shown in Figure 2, the initial spectrum of (**3**) (note: the

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spectrum of **(4)** is not shown) is composed of two major absorption bands: a narrower band with a maximum at 280 nm and a broader band between 325 and 450 nm.
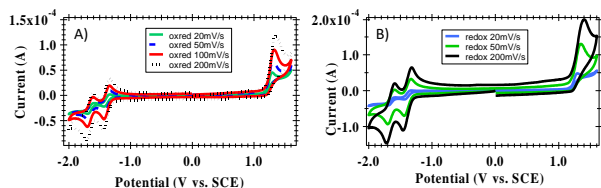

Figure 1: Cyclic voltammetry studies of (3) as a 1 mM solution in MeCN with 0.1 M TBAP in a 3-electrode configuration cell using WE as a glassy carbon, CE platinum wire and SCE as the reference electrode, at different scan rates from 20–750 mV s^{-1}. Electrochemical window A) 0/1.5/-2/0 and B) 0/-2/1.5/0.

Following the results of the cyclic voltammetry study, it was realized that there was the potential for the generation of a fluorescent and electrochromic radical anion and, therefore, a charge of -1.5 V (vs. SCE) was applied for 3600 s. 15s after commencing the experiment, the spectra changed, with a notable decrease in intensity in the broad band (between 325-450 nm) and two new absorption bands appearing at 480 and 620 nm, respectively. There was a bathochromic shift of the band at 250 nm to 280 nm. Such observations can be interpreted as the disappearance of the neutral compound and the emergence of a negatively charged species. This interpretation is corroborated by the TD-DFT calculation that assign the decreasing band between 325-450 nm to the neutral compound and the emerging bands at 480 and 620 nm to the negatively charged species (Table s3, Fig s10) The intensity of the absorption bands at 480 and 620 nm increase until reaching 3000s. The oxidation process of **(3)** was also studied (Scheme s.4).
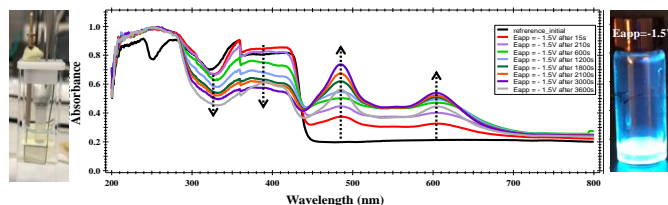

Figure 2: Spectroelectrochemical experiments of **(3)** 1 mM solution in MeCN with the electrolyte TBAP (0.1 M) in a 3-electrode configuration cell, WE platinum grid, CE platinum wire, reference electrode Ag/AgCl. Applied Potential -1.5 V and the spectrum measured over the following period: 15, 210, 600, 900, 1200, 1800, 2100, 2700, 3000 and 3600 s.

The normalized absorption spectra for **(3)** in toluene, chloroform, acetonitrile and ethanol are shown in Figure 3 A)) and contain three main absorption bands: around 280, 390 and 410 nm. These bands are in good agreement with the TD-DFT calculation results, where the lower energy vertical transitions at 401 nm and 403 nm (mainly of HOMO->LUMO character) were calculated for compounds **(3)** and **(4)**, respectively (Figure s.19 and Tables s.9 and s.14). A slight hypsochromic shift is observed as the polarity of the solvent increases which is consistent with n→π* electronic transitions.[18] The calculated electronic density rearrangement that occurs upon the S$_0$->S$_1$ transitions is depicted in Figure 4. It represents the difference between the electronic densities of the states involved in the

transitions, and is in line with the experimental observation, showing a depletion of electronic charge on the oxygen and nitrogen atoms. The pattern is similar for both compounds and the OCH$_3$ group in **(3)** does not seem to significantly change the electronic distribution.

Figure 3: Normalized absorption (A) and emission (B) spectra (λ_{exc}=390 nm) of **(3)** in different solvents.
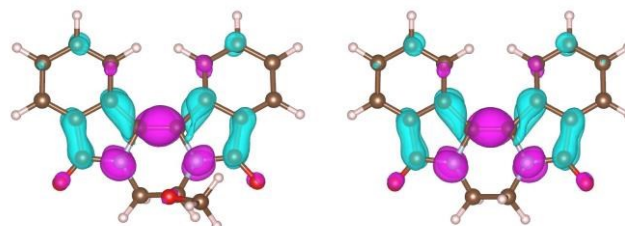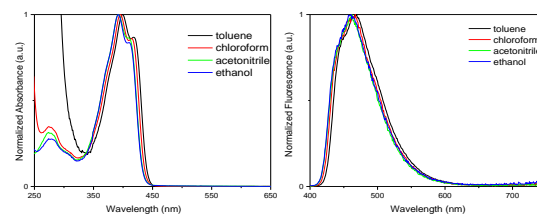

Figure 4: Contour plots of the electron density difference (Δρ) upon the lowest energy excitation S$_0$->S$_1$ of the neutral compounds **(3)** (on the left) and **(4)** (on the right) in acetonitrile solution. Magenta and blue isosurfaces represent negative (loss of electrons) and positive (electron gain) values, respectively.

Figure 3B shows the normalized emission spectra in the same solvents (λ_{exc} = 390 nm) with a maximum around 465 nm (Table s.3). Compound **(3)** exhibits a bright blue luminescence with a high quantum yield of 0.56 that was determined by the comparative method using 7-(diethylamino)-4-methylcoumarin (Coumarin 1) (Φ= 0.5) in ethanol as reference.[19] Compound **(4)** possessed a comparable behavior to **(3)** with a quantum yield of 0.60.

The electroluminescence properties of compound **(3)** were assessed in a simple organic light-emitting diode (OLED) structure, where the active layer was made of neat compound **(3)** deposited by spin-coating, which showed acceptable performance. In particular, a maximum luminance of 44 cd/m^2 was achieved with a luminous efficiency of 0.04cd/A, a result that can be optimized (See the SI for details of the device preparation and performance). The stability of these compounds in films still required further optimization (see SI). Aging of the thin films leads to bleaching under environmental conditions. Thin films of these compounds tend to crystallize over time, a process that is slower for compound **(3)**, which we attribute to the presence of the methoxyl group.

In order to gain further insights into the applicability of these compounds as OSC in OTFTs we used Marcus theory[20] and conducted a number of key calculations to determine their reorganization energies (λ, see Supporting Information for a detailed discussion) and to estimate the mobility of compound **(3)**, for which we have an X-ray crystal structure data available (unfortunately, we did not have an X-ray crystal structure for **(4)**) . Reorganization energy is a metric affording insight into

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electron and hole mobility in OSC materials.[21] and accounts for the energetic cost of the geometry adjustment on the hole/electron transport process. The lower the λ the smaller the energy cost of the geometry relaxations and the higher the electron transfer rate.[21] DFT calculations of λ for OSC materials are rare. In our studies we calculated λ_h to be 0.453 eV and λ_e to be 0.380 eV for **(3)** and 0.421 and 0.364 eV for **(4)**. Since for both compounds λ_h and λ_e have almost similar values we can anticipate that the compounds are likely to show ambipolar behavior. However, since the λ_e values are slightly smaller it can be assumed that the compounds will have a leaning towards n-type. The calculated electron carrier mobility μ_- and the hole carrier mobility μ_+ for compound **(3)** were 0.731 and 0.379 cm^{2}V^{-1}s^{-1}, respectively showing the compound are likely to show ambipolar behavior with a leaning towards n-type semiconductor (corroborating the results obtained for the reorganization energies above)(see the SI). Moreover, comparing the results for **(3)** and **(4),** the lower λ values of **(4)** suggest that it should have better mobility than **(3)**. This could be due to the presence of the stereogenic center in **(3)** and an electron-donating methoxyl group.

In conclusion, we have synthesized two novel lightweight pentacyclic imide compounds **(3)** and **(4)** with interesting optoelectronic and electrochemical properties. Both compounds showed very good electrochemical properties with energy gaps of 2.60 eV and 2.54 eV, respectively, indicating that they are suitable OSC compounds. Compound **(3)** showed very interesting fluorescence properties, with two new absorption bands at 480 and 620nm appearing upon its reduction. Both compounds showed reasonable fluorescence efficiency in solution. The preliminary tests on OLEDs based on compound **(3)** suggest these are interesting compounds for optolectronic applications. Reorganization energy and carrier mobility calculations confirmed the suitability of both compounds as OSC active components (λ_h = 0.453 eV and λ_e = 0.380 eV and μ_- = 0.731 and μ_+ = 0.379 cm^{2}V^{-1}s^{-1} for **(3)** and λ_h = 0.421 and λ_e = 0.364 eV for **(4)**), with a slight predominance for n-type semiconductor behavior. Work is on-going on the synthesis of further derivatives with potentially superior optoelectronic properties, charge mobilities and on improving their stability.

Conflicts of interest

There are no conflicts to declare.

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Ambipolar Pentacyclic Diamides with Excellent Electrochemical and Optoelectronic Properties

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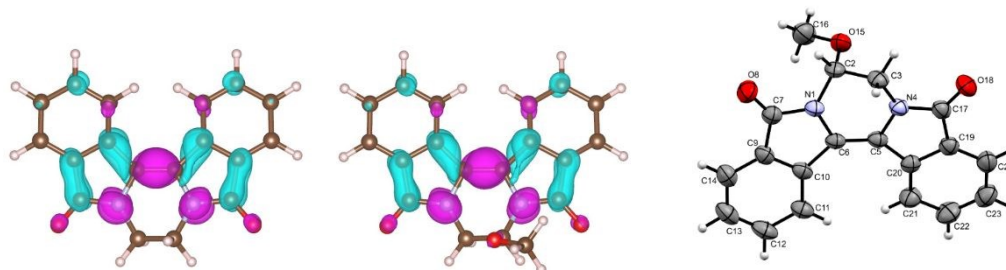
We report on the application of novel small-molecule highly crystalline pentacyclic diamides possessing significant OTFT and OLED potential.