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Pyrrole-cored push–pull single chromophore

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A B S T R A C T

We report a straightforward synthesis toward pyrrole-cored push-pull single chromophore in which the electron-donating (D) units are pyrrole groups and electron-withdrawing (A) moieties are diketone groups. Optical and electrochemical properties of the novel pyrrole-based building block embedding carbonyl functionalities were studied in detail. On the redox behaviors, this resulting material not only possesses low-lying LUMO but also displays high-lying HOMO with fully reversible p-and n-doping, which can establish it as a good candidate for use as electron/hole-transporting material in optical and electro-optical applications.

1. Introduction

One of the most important developments in the synthesis of π-conjugated materials has been the utilization of donor–acceptor architectures within the backbone since the built-in intermolecular charge transfer can facilitate ready manipulation of the electronic structure (HOMO/LUMO levels), leading to small band gap semiconducting materials[1–6] with relatively high charge carrier mobilities.[7–14] Furthermore, such compounds are potentially; (i) intrinsically good electrical conductors or semiconductors without the need of any chemical or electrochemical doping reaction, (ii) transparent in either the neutral or doped state and (iii) of interest as new polymeric materials for nonlinear optics.[15]

Among the various π-conjugated materials, the thiophene, oligothiophenes, and derivatives have most widely been the electron-donating moieties used in constructing donor–acceptor conjugated materials.[1–3,5] Although pyrrole-based materials have also attracted strong attention due to their high electrical conductivity, thermal, and environmental stabilities,[16] to the best of knowledge, there exist no examples of the pyrrole materials with push-pull architecture within a single chromophoric unit.

Herein, we present the synthesis and characterization of a push–pull material based on pyrrole via intramolecular Friedel–Crafts acylation, which is the first example of pyrrole-cored push–pull-type single chromophore system.

2. Synthesis and characterization

The facile synthesis of the target molecule toward the desired bis-carbonyl-bridged 1-(4-octyl-phenyl)-2,5-diphenyl-1*H*-pyrrole compound is outlined in Scheme 1. 2,2′-(1,3-Butadiyne-1,4-diyl)bisbenzoic acid dimethyl ester (**3**) was easily prepared in three steps (isolated overall yield = 72%).[17] The cycloaddition reaction of **3** with *p*-octylphenylamine gave 2,2′-[1-(4-octylphenyl)1-*H*-pyrrole-2,5-diyl]bisbenzoic acid dimethyl ester (**4**) using copper(I) chloride. Double intramolecular Friedel–Crafts acylation was performed by the treatment of the diester **4** with concentrated sulfuric acid 165 °C,[18,19] no product was isolated. This failure is presumably due to the instability of the pyrrole moieties under the acid and high-temperature condition. An alternative ring closure of the diester **4** to prepare the target molecule was therefore sought, probably it can be achieved by means of a combination of saponification and Lewis acid-promoted intramolecular cyclization. Thus, **4** was hydrolyzed by treatment with KOH as strong base to obtain the corresponding benzoic acid **5** which is a key intermediate material of the target. Compound **5** was treated with oxalyl chloride, and then intramolecular Friedel–Crafts acylation using aluminum chloride gave the desired pyrrole-based building with diketone **6** (11%). It has been reported[20] that the method for the synthesis of the starting five-membered heterocycle consisting of intramolecular cyclization of 2-hetarylbenzoic acids and their derivatives under various conditions suffer from a number of drawbacks such as low accessibility of these benzoic acids, sometimes unpredictable reaction route,[21] and relatively low yields, most likely resulting in the observed low yield for the last step of the synthesis of **6**.

The absorption behavior of **6** was measured in solvents of varying polarity in order to investigate the solvatochromism of these donor(D)–acceptor(A) molecules. Two prominent absorption bands along with a shoulder are observed in the spectra of **6** in all solvents: a broad lower intensity band at 500–520 nm range, a higher intensity band at 408–422 nm range, and a shoulder at 429–445 nm range. The high-energy absorption band can be associated with π–π^* transitions of the D–A molecules. As depicted in Figure 1a, the absorption maxima of **6** recorded in various solvents

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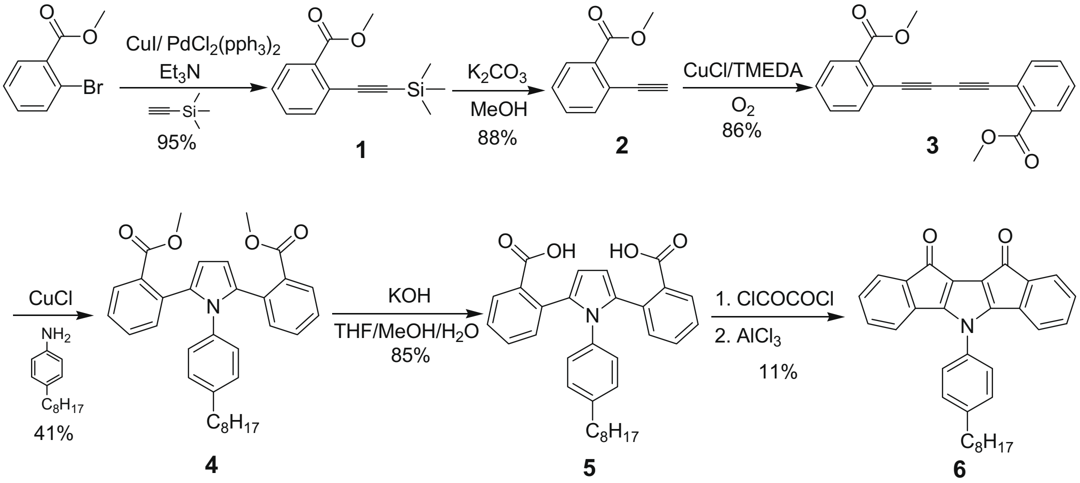

Scheme 1. Synthesis of pyrrole-based material with diketone.

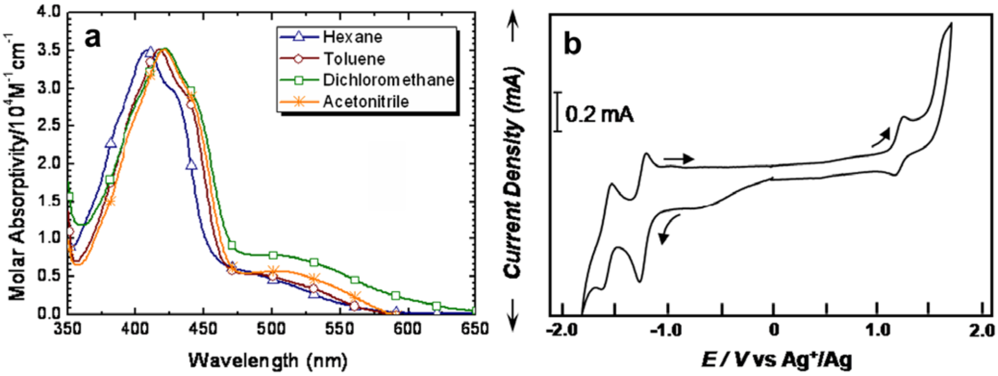

Figure 1. UV–vis absorption spectra of **6** in solvents of varying polarity (a) and cyclic voltammogram of **6** in acetonitrile solution (b).

reveal moderate bathochromic shift upon increasing the polarity of the solvent from 408 nm in hexane to 422 nm in acetonitrile. This indicates that this molecule possesses unambiguously intramolecular charge transfer (ICT) from the push (pyrrole) to the pull (ketone) unit.[22–26] However, the color change of **6** is not observable by the human eye as a function of solvent polarity. It is known that larger solvatochromic shifts are observed in the PL emission spectra compared to those in the absorption spectra because of an excited state with much stronger ICT character and larger dipole moments relative to the ground state.[27,28] However, the PL properties of **6** cannot be analyzed in various solvents since the observed PL intensities are too low due to internal quenching units (two ketone).

3. Photophysical properties

The redox behavior of **6** was investigated by cyclic voltammetry (CV) against Ag/Ag+. As shown in Figure 1b, **6** exhibits clear reversibility in both the p-doping and n-doping processes, with two reduction peaks −1.25 and −1.61 V, which can presumably be assigned to the reduction of the diketone to the quinoidal dianion, and an oxidation peak at 1.29 V. The reduction and oxidation onsets occurred at −1.15 and 1.18 V, from which the LUMO and HOMO energy levels were estimated to be 3.25 and 5.58 eV, respectively. The LUMO levels of **6** are somewhat raised in comparison with LUMO levels of phenylene-based materials with diketone reported previously.[18,19] A likely rationale for this is the inductive effect of the nitrogen atom in the chromophore. This corresponds to an electrochemical bandgap of 2.33 eV, which is slightly larger than its optical bandgap determined from the onset of maximum absorption wavelength (~2.15 eV). It has been demonstrated that the electrochemical bandgaps in general are higher than the optical bandgaps.[29–31] The relatively high EA is lower than that of 2-(4-biphenylyl)-5-(4-*tert*-butylpehnyl)-1,3,4-oxadiazole (PBD) (ca. −2.4 eV), one of the most widely used electron injecting/transport materials,[32] and comparable with that of CN-PPV (3.10 eV)[33] which shows good electron-transporting ability in polymeric LEDs. Therefore, **6** which shows reversible reduction is a promising electron-transporting material.[34,35] Moreover, the HOMO energy levels of **6** matches well with one of the most widely used hole-transporting materials ((4,4′-bis(4-(*N*-(1-naphthyl)-*N*-phenylamino)-phenyl)biphenyl (5.46 eV)).[36] Thus, **6** also holds potential as a hole injecting and hole transport material in OLEDs.

In summary, the pyrrole-based building block with diketone bridge **6** as push-pull-type material was successfully prepared via intramolecular Friedel–Crafts acylation with 2,2′-[1-(4-octylphenyl)1-*H*-pyrrole-2,5-diyl]bisbenzoic acid (**5**). The compound **6** shows good processability from solution. On the redox behaviors, **6** not only shows low-lying LUMO but also displays high-lying HOMO with fully reversible p- and n-doping. Such attractive properties of **6** can establish it as a promising candidate for use in optical and electro-optical applications. A detailed investigation of various devices fabricated from **6** is in progress and will be reported in a future Letter.

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Supplementary data

Supplementary data (full experimental details for the synthesis of all new materials are available. Supplementary data associated with this article can be found, in online version) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.029.

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