Synthesis of mesogenic phthalocyanine-C$_{60}$ donor–acceptor dyads designed for molecular heterojunction photovoltaic devices

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Abstract

A series of phthalocyanine-C$_{60}$ dyads 2a–d was synthesized. Key steps in their synthesis are preparation of the low symmetry phthalocyanine intermediate by the statistical condensation of two phthalonitriles, and the final esterification of the fullerene derivative bearing a free COOH group. Structural characterization of the molecules in solution was performed by NMR spectroscopy, UV–vis spectroscopy and cyclic voltammetry. Preliminary studies suggest formation of liquid crystalline (LC) mesophases for some of the prepared dyads. To the best of our knowledge, this is the first example of LC phthalocyanine-C$_{60}$ dyads.

Introduction

Among sustainable energy technologies, photovoltaic (PV) conversion of solar energy is considered as a promising solution. Although currently the market is dominated by inorganic PV devices, development of organic PV materials is driven by their compatibility with solution processing and hence the potentially low cost of large-scale production by printing technologies [1-3]. One of the most popular concepts in the design of organic PV devices is the “bulk heterojunction” architecture, featuring blends of the two immiscible materials: a donor and an acceptor of electrons [4-7]. After absorption of a photon, an initially formed exciton is dissociated at the donor/acceptor interface into a positive charge (hole) and a negative charge (electron), which are transported to the electrodes. Hence, a critical issue in bulk heterojunction PV devices is the control of morphology of materials, in order to provide both the efficient exciton generation and the rapid charge carrier transport. The logical step in the development of this architecture is “molecular heterojunction”, that is, creation of covalent link-
Figure 1: Phthalocyanine-C$_{60}$ dyads 2a–d described in this paper, C$_{60}$-derivative 1 (PCBM) and previously reported mesogenic phthalocyanine 3.

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Phthalocyanines (Pc) have found a number of industrial applications as dyes and pigments due to their bright blue or green colors combined with extraordinary thermal and photochemical stability [30]. Phthalocyanines bearing flexible peripheral substituents form columnar mesophases [8,31], which demonstrate very efficient charge transport along the columns [32,33]. A unique combination of properties makes phthalocyanines excellent candidates as active materials for photovoltaic devices.
mesophases [45]. To this end, we envisaged the variation of the linker between the fullerene and the phthalocyanine unit.

The synthesis of dyads 2a–d is summarized in Scheme 1 and Scheme 2. The key step, which also represents a bottle-neck in terms of yield (see below), is the preparation of the low-symmetry phthalocyanines 4a–d. To this end, we originally decided to explore the statistical condensation of phthalonitriles 5 and 6a–d (Scheme 1). Previously, synthesis of 4-alkoxyphthalonitriles such as 5 via aromatic nucleophilic substitution in 4-nitrophthalonitrile with the corresponding alcohols in the presence of LiOH in DMSO was reported [46]. However, the yields of phthalonitriles 5 were moderate (below 50%) and their separation from multiple side products was cumbersome. Hence, we preferred to prepare 5 (80% yield) by Williamson reaction between phenol 7 and bromide 8. The latter was synthesized from the corresponding commercially available alcohol by the well-known general method (CBr₄/PPh₃) [47]. A similar procedure was then used to synthesize phthalonitriles 6a–d (80–86% yield) starting from the corresponding commercially available ω-bromoalcohols.

Several strategies for the synthesis of low-symmetry A₃B phthalocyanines (where A and B refer to the chemically different isoindole units comprising the phthalocyanine core) were reported earlier, including expansion of subphthalocyanines or solid-phase synthesis on polymer supports [48]. However, operationally simplest and shortest route is the statistical condensation of the two different phthalonitriles. This method inevitably produces a mixture of the desired A₃B phthalocyanines with the products of compositions A₄, A₂B₂, AB₃ and B₄. In theory, 3 : 1 molar ratio of the two dinitriles is required to access A₃B products. However, using larger excess of one of dinitriles (often 9 : 1 stoichiometry is used) is more practical. Although the amount of the A₄ phthalocyanine in the reaction mixture grows, the formation of cross-condensation products other than A₃B is essentially suppressed (see Figure SI2 in the Supporting Information for the graphical presentation of the product distribution). Hence, the isolation of the desired A₃B is limited to the separation from the A₄. Another factor that facilitates the separation by chromatography is rather different polarity of the substituents on A and B units. In our case, the oligomethylene linker with a terminal OH group is much more polar than the bulky swallow-tail alkyl group, and we did not expect difficulties in the separation of condensation products.

However, attempted condensation of 5 and 6a–d gave no desired phthalocyanine derivative. We reasoned that the unprotected OH group in one of the reaction components may affect the condensation, and converted alcohols 6a–d into acetals 9a–d (84–93% yield) by treatment with an excess of meth-
The structure of the phthalocyanines 4a–d was confirmed by 1H and 13C NMR, and HR-MALDI mass spectrometry. 1H NMR spectra of low-symmetry phthalocyanines 4a–d and 10a–d in CDCl3 closely resemble those of 3 and feature a series of three unstructured multiplets from the protons of 1,2,4-substituted benzene rings. Inner-core protons in 4a–d and 10a–d are observed as a broad and concentration-sensitive high-field signal. It should be noted that 3 (as well as any phthalocyanine derivative prepared from a 4-substituted phthalonitrile) represents a mixture of four regioisomers [48,53], while lower-symmetry 4a–d and 10a–d are actual mixtures of as many as eight regioisomers each. This greatly complicates their NMR spectra (see Supporting Information). Furthermore, each regioisomer is a mixture of different diastereoisomers due to the presence of the asymmetric carbon atom in every peripheral substituent. However, although 2-decyloctadecyl substituents in 3 and 10a–d are formally chiral, they should actually be treated as pseudo-achiral since the difference between the two of the substituents at the asymmetric carbon (the two linear alkyl groups of different length) is very small. As was shown previously, the complex diastereomeric composition does not influence the behavior of phthalocyanines bearing similar swallow-tail branched alkyl chains [46,54-57]. UV–vis absorption spectra of 4a–d (Figure 2) are characteristic for metal-free phthalocyanine derivatives: they feature two intense long-wave absorption bands (termed Q-bands).

In the final synthetic step, reaction between 4a–d and the acid 11 (prepared by acid-catalyzed hydrolysis of the commercially available methyl ester 1, PCBM) [10,58] afforded the corresponding dyads 2a–d (Scheme 2). Although in general esterification appears as a trivial synthetic transformation, esterification of 11 is greatly complicated by its poor solubility in virtually all organic solvents. After some experimenting, we found that the classical dicyclohexylcarbodiimide/N,N-dimethylaminopyridine (DCC/DMAP) protocol gives the best results, provided the acid 11 was first sonicated in o-dichlorobenzene for two hours prior to reaction, and then an alcohol 4a–d, DCC and DMAP were added to the reaction mixture. After purification by column chromatography, the dyads 2a–d were isolated in yields up to 45%. Again, the relatively modest yields are comparable with or superior to those previously reported for the esterification of poorly soluble acid 11 with various alcohols [22,50,59].

The structure of dyads 2a–d was confirmed by NMR, MALDI MS and UV–vis absorption spectroscopy. 1H NMR spectra of the dyads 2a–d essentially correspond to the superposition of the spectra of the phthalocyanine 4a–d and PCBM (1), with the exception of the signal of CH2OC=O in dyads 2a–d (ca. 4.10 ppm), which is shifted downfield vs. the signal of CH2OH in phthalocyanines 4a–d (ca. 3.80 ppm). 13C NMR spectrum of the dyad 2c also essentially represents a superposition of the spectra of phthalocyanine 4e and PCBM (1). However, its detailed interpretation is greatly complicated because of a large number of signals, broadening of the signals due to the complex isomeric composition of phthalocyanine (see above), and overlaps of signals (see Supporting Information for the original NMR spectra). For this reason, only selected 13C chemical shifts are given in the Experimental Part. UV–vis absorption spectra of the dyads 2a–d also appear as superposition of the spectra of 4a–d and 1: next to the intense Q-band (maxima at 670 and 707 nm) and B-band (between ca. 300 and ca. 450 nm) of phthalocyanine moiety, very strong high energy absorption of the cyclopropanated C60 derivative with the maximum at ca. 260 nm is observed (Figure 2).
Cyclic voltammetry measurements of dyads 2a and 2d in CH$_2$Cl$_2$ produced essentially identical results. Wave potentials do not change upon elongation of the spacer between the donor and the acceptor (Table 1). Furthermore, the voltammograms effectively correspond to the superposition of those for PCBM (1) and the phthalocyanine 3, and do not display supplementary waves (Figure 3). The reduction part of the voltammograms of 2a,d displays five quasi-reversible reduction waves, three due to the C$_{60}$ moiety and two due to the phthalocyanine fragment. In the oxidation part of the voltammograms of 2a,d, several poorly resolved waves identical to those of phthalocyanine 3 are observed at potentials up to +1.6 V vs. saturated calomel electrode (SCE). These observations, together with UV–vis spectra, suggest the absence of intramolecular charge transfer in the ground state for dyads 2a–d.

Preliminary investigation of the dyads 2a–d by polarized optical microscopy (POM) showed that the length of the spacer between the phthalocyanine and the fullerene moieties significantly affects the thermotropic properties of the material. Dyads 2a,b are liquid at room temperature, while dyads 2c,d display at room temperature fluidic birefringent textures confirming the occurrence of liquid crystalline (LC) mesophases. Upon heating, transitions to isotropic liquid were observed at 120 °C and 90 °C for 2c and 2d, respectively. For 2c this transition was only detectable by POM and not by differential scanning calorimetry (DSC), while for 2d DSC on heating revealed an endothermic peak at 90 °C [enthalpy 2.7 kJ/mol] in perfect agreement with POM observation. The small enthalpy value supports the transition from LC mesophase to isotropic liquid. However, assignment of the nature of LC mesophases for 1c,d from the available data was not obvious, since the textures observed by POM were not characteristic. The major conclusion is nonethe-

- less that the length of the spacer in 2a–d between the C$_{60}$ fragment and the mesogenic phthalocyanine moiety decisively affects the supramolecular structure of the material.

Conclusion

We report the first example, to the best of our knowledge, of mesogenic phthalocyanine-C$_{60}$ dyads. The key step in their synthesis is the preparation of the low-symmetry phthalocyanines, bearing three mesogenic swallow-tail substituents and an OH-terminated polymethylene linker. These key intermediates were synthesized by experimentally simple statistical condensation of two phthalonitriles, giving comparatively high yields (up to 24%) for this type of reaction. Upon the favorable combination of the length of the linker with the length of peripheral substituents on the phthalocyanine, bulky C$_{60}$ moiety can be accommodated in the LC mesophase. Detailed analysis of this supramolecular organization, as well as deeper insight in the structure-property relationships of dyads 2, will be the subject of a separate publication. Other objectives of our ongoing research include: studies of macroscopic alignment in films of dyads 2, studies of charge carrier mobility in aligned films, and fabrication and evaluation of photovoltaic devices.
**Experimental**

**General details.** All chemicals were purchased from Aldrich, Acros or TCI and used without further purification. Acid 11 was prepared according to the published procedure [10]. TLC was performed on precoated plates with silica gel 60 F254 (Merck), visualization with UV (λ = 254 nm). Column chromatography was performed on silica gel (0.040–0.063 mm, Macherey–Nagel). 1H NMR and 13C NMR spectra were recorded on a Bruker Avance 300 or Varian VNMRS 400 spectrometers; chemical shifts are given in ppm relative to Me4Si (internal standard); coupling constants J are given in Hz. MALDI mass spectra were recorded on a Waters MALDI-QTOF Premier, using a 350 mW laser with dithranol (1,8-dihydroxy-10H-anthracen-9-one) as matrix for phthalocyanines and with DCB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidenen]malonitrile) as matrix for fullerene derivatives; EI and ESI mass spectra were recorded on a Waters AutoSpec 6. UV–Visible absorption spectra were recorded on a HP 8453 spectrophotometer in a quartz cell (optical path of 1 cm). For POM experiments, a NIKON Eclipse 80i microscope equipped with a digital camera DS Camera Head D5-5M was used; chemical shifts are given in ppm relative to MeSi (TMS) as internal standard; coupling constants J are given in Hz.

**Electrochemistry.** Cyclic voltammetry experiments were performed with a computer controlled Autolab potentiostat. Measurements were carried out at room temperature in a three-electrode single-compartment cell (10 mL), in CH2Cl2 solutions (concentration 10−4 M), containing Bu4NPF6 (0.1 M) as supporting electrolyte, at a scan rate of 100 mV s−1. A glassy carbon, polished by a slurry-suspension of alumina on microcloth and washed by Milli-Q water before each experiment, was used as a working electrode. A spiral platinum wire was employed as counter electrode and an Ag/AgCl/KCl(sat) used as a reference electrode. All potentials are reported versus the ferrocene/ferrocinium (Fc/Fc+) couple (E°Fc/Fc+ = 0.425 V vs. saturated calomel electrode (SCE)) and Ag/AgCl (E°Ag/AgCl = 0.197 V vs. SCE). Before each measurement, solutions were deaerated by 20 min nitrogen bubbling.

4-(2-Decyltetradecyloxy)phthalonitrile (5). To a solution of phenol 7 (1.80 g, 12.5 mmol) and bromide 8 (4.18 g, 10 mmol) in dry DMF (60 mL) was added dry K2CO3 (1.72 g, 12.5 mmol). The mixture was stirred at 90 °C under Ar for 7 h. After cooling to r.t., the mixture was poured into water (60 mL) and extracted with AcOEt (3 × 200 mL). The combined organic layers were washed with aqueous NaHCO3 (5%), dried with MgSO4 and concentrated in vacuum. Column chromatography (SiO2, CH2Cl2) afforded pure 5 as a light yellow solid (4.81 mg, 80%); Rf 0.7 (CH2Cl2). Analytical data identical to those previously reported [46].

4-{10-[(2-Methoxyethoxy)methoxy]decyloxy}phthalonitrile (9e). A solution of phthalonitrile 6e (570 mg, 1.47 mmol) and i-Pr2EtN (0.77 mL, 4.5 mmol) in CH2Cl2 (30 mL) was treated dropwise with MEMCl (0.33 mL, 2.94 mmol) and the resulting mixture was stirred overnight at r.t. The mixture was then treated with aqueous saturated NaHCO3 (35 mL); the organic layer was separated, the aqueous layer was extracted with CH2Cl2 (2 × 40 mL), combined organic layers were dried over MgSO4 and evaporated. Column chromatography of the residue (CH2Cl2/AcOEt 4 : 1, Rf 0.69) afforded 9e (479 mg, 84%) as a light yellow solid; mp 43 °C; Rf 0.64 (CH2Cl2/AcOEt 9 : 1); 1H NMR (300 MHz, CDCl3, 25 °C): δ = 7.68 (6H, 2H, ArH); 7.24 (4H, 2H, ArH); 6.49 (2H, OCH3O); 4.03 (t, J = 6.5 Hz, 2H, CH2O); 3.68 (t, J = 5.1 Hz, 2H, CH2O); 3.52–3.60 (4H, 4H, ArOCH2); 1.26–1.64 (m, 14H); 13C NMR (100 MHz, CDCl3, 25 °C): δ = 162.2, 135.1, 119.5, 119.3, 117.4, 115.7, 115.3, 107.0, 95.5, 71.8, 69.3, 67.9, 67.6, 67.0, 59.0, 29.7, 29.4, 29.4, 29.2, 28.7, 26.2, 25.8; HR-MS (EI): m/z calcd. for C22H22N2O2 ([M]+): 388.2362, found 388.2374.

2-{10-[(2-Methoxyethoxy)methoxy]decyloxy}-9(10),16(17),23(24)-tri(2-decyltetradecyloxy)-29H,31H-phthalocyanine (10c). Li (125 mg, 17.7 mmol) was dissolved under Ar in n-pentanol (10 mL) and the mixture was heated to reflux until Li was completely dissolved. After cooling to r.t., a solution of phthalonitriles 5 (3.41 g, 7.11 mmol) and 9c (305 mg, 0.79 mmol) in n-pentanol (15 mL) was added dropwise and the mixture was heated to reflux overnight. After cooling to r.t., AcOH was added dropwise until pH 5–6 was reached. The green solid was filtered and extensively washed with MeOH. Column chromatography of the residue afforded first 3 (eluted with CH2Cl2, 1.76 g, 50%) and then 10c (eluted with CH2Cl2/AcOEt 1 : 1, 347 mg, 24%). Green solid; Rf 0.75 (CH2Cl2/AcOEt 1:1). 1H NMR (300 MHz, CDCl3, 25 °C): δ = 8.50–8.90 (4H, 4H, H-H); 7.30–7.60 (m, 4H, 4H, H-H); 4.71 (2H, OCH2O); 4.25–4.50 (5H, 8H, ArOCH2); 3.65–3.80 (4H, 4H, ArOCH2OCH2); 3.58–3.63 (m, 2H, 2H, OCH2OCH2); 3.36 (s, 3H, MeO); 2.10-2.23 (m, 5H, 5H, ArOCH2CH2 + ArOCH2Cl); 1.15–1.90 (m, 13H); 0.85 (t, J = 6.8 Hz, 18H); –2.84 (s, 2H, NH); 1H NMR (100 MHz, CDCl3, 25 °C): δ = 160.2 (br); 147.0 (br); 136.6 (br); 127.8 (br); 122.2 (br), 117.0 (br), 104.0 (br), 94.6 (OCH2O), 70.9 (br, CH2O), 70.7 (br, CH2O), 67.4 (br, CH2O), 66.9 (CH2O), 65.7 (CH2O), 58.0 (MeO), 37.5 (br), 30.5–31.0 (several CH2), 28.3–29.4 (several CH2), 26.3 (CH2), 25.8; HR-MS (EI): m/z calcd. for C22H22N2O2 ([M]+): 388.2362, found 388.2374.
25.2–25.5 (several CH2), 21.5–21.8 (several CH2), 13.1 (Me); HR-MS (MALDI): m/z calcd. for C_{118}H_{190}N_{10}O_{7} ([M]^+) 1831.4757, found 1831.4748.

2-(10-Hydroxy-decylxy)-9(10),16(17),23(24)-triti(2-decyll-tetradecyloxy)-29H,31H-phthalocyanine (4c). A stirred solution of the phthalocyanine 10c (275 mg, 0.15 mmol) and PPTS (188 mg, 0.75 mmol) in t-ButOH (20 mL) was heated to reflux overnight. After cooling to r.t., the reaction mixture was concentrated in vacuum. The resulting solid was suspended in MeOH (50 mL), then filtered, extensively washed with MeOH and dried to give 4c (261 mg, 100%). Green solid; ^1H NMR (300 MHz, CDCl3, 25 °C); δ = 8.90–9.20 (m, 4H), 8.45–8.80 (m, 4H), 7.50–7.75 (m, 4H), 4.35–4.55 (m, 8H, ArOCH2), 3.72 (t, J_{3H,3H} = 6.0 Hz, 2H, C(2)OH), 2.03–2.20 (m, 5H, ArOCH2CH2 + ArOCH2CH4), 1.10–1.95 (m, 134H), 0.80–0.93 (m, 18H), −3.07 (s, 2H, NH); 13C NMR (100 MHz, CDCl3, 25 °C): δ = 173.1 (C=O), 160.3 (br, arom. C–O), 79.7 (fullerene C(sp^3)), 71.8 (br, CH2O), 68.4 (br, CH2), 64.1 (CH_2OC=O), 51.7 (PhC), 33.5 and 34.0 (CH_2C=O and PhCCH2); HR-MS (MALDI): m/z calcd. for C_{114}H_{182}N_{10}O_{7} ([M]^+) 1743.4240, 1743.4240.

Phthalocyanine-C_{60} dyad 2c. A solution of the phthalocy-
anine 4c (64 mg, 0.037 mmol) and the acid 11 (50 mg, 0.056 mmol) in o-dichlorobenzene (7 mL) was sonicated for 2 h. After cooling to 0 °C, DCC (31 mg, 0.15 mmol) and DMAP (18 mg, 0.15 mmol) were added, the mixture was allowed to reach r.t. and was stirred overnight. The resulting mixture was concentrated and the residue was purified by column chromatography (CHCl3/CH2Cl2/hexane 3 : 2) to give 2c (46 mg, 47%). Green solid; 

Supporting Information
Experimental procedures and analytical data for derivatives 2a,b,d, 4a,b,d, 6a–d, 9a,b,d, 10a,b,d.

Supporting Information File 1
Experimental details
[http://www.beilstein-journals.org/bjoc/content/ supplementary/1860-5397-5-49-S1.doc]

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