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Triaryl-substituted pyrrolo-*p*-phenylene-linked porphyrin-fullerene dyads: Expanding the structural diversity of photoactive materials



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1. Introduction

Porphyrin-fullerene dyads can form a charge separated (CS) state through the intramolecular electron transfer processes upon photoexcitation, ^{1–4} and have been considered as promising candidates for the materials for photovoltaic^{5.6} or photo-redox-catalytic applications.^{6–8} Recently, Buldum and Reneker predicted that a rigid *p*-phenylene linked donor-acceptor dyad should secure dual-channel film morphology favoring the charge transport after the initial step of the charge separation.⁹ In our recent work, we demonstrated a photovoltaic activity of a similar *p*-phenylene linked porphyrin-fullerene dyad **1aa** which exhibited the photocurrent of up to $4 \,\mu A \, \mathrm{cm}^{-2}.^{10}$

The performance of the photovoltaic devices based on compounds of this class of dyads should depend on the electronic and morphological parameters on the molecular level. The most straightforward route for the tuning the electronic structure of the porphyrin-fullerene dyad is to vary the substituents at the porphyrin core, which should affect the Gibbs free energy for the charge recombination and the electronic coupling between the

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ABSTRACT

A protocol for the synthesis of pyrrolo-*p*-phenylene-linked porphyrin-fullerene dyads suitable as photoactive materials was developed. The sequence of aziridination – aziridine ring opening – 1,3-dipolar cycloaddition reactions enabled us to provide structural variability both to the porphyrin core and to pyrrole linker, which facilitates designing the electronic structure and morphological parameters of the dyads. The key porphyrin building blocks, nitro-porphyrins, were synthesized by a stochastic cyclocondensation of arenecarbaldehydes with *p*-nitrophenyl(dipyrrolyl)methane.

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donor and acceptor moieties, both of which are the important parameters in Marcus theory of charge transfer. Within the class of the dyads, the simplest representative of which is compound **1aa**, the morphology of the photoactive films made from such porphyrin-fullerene dyads is expected to be varied by the changes in the alkyl chains in the ester fragments because of the associated changes in the intermolecular interactions between the dyads as well as in their steric sizes.

In the present study, we focus on the series of porphyrinfullerene dyads **1** bearing various substituents in *p*-position of *meso*-phenyl rings (Scheme 1), including strong π -donor (CH₃O), weak σ -donor (CH₃), π -donor and σ -acceptor (Br) along with strong σ -acceptor (CF₃), and alkyl groups of various lengths in the ester fragments containing ethyl, *n*-butyl, *n*-hexyl and *n*-octyl groups, and develop our synthetic methodology for the preparation of pyrrolo-*p*-phenylene-linked porphyrin-fullerene dyads so that the structural parameters responsible for the perturbation of the electronic structure of the dyad as well as for the morphology of the film composed of the dyads can be manipulated. In the course of the exploration of the synthetic routes, we found that nitroporphyrins are convenient building blocks to incorporate variable aryl groups into the porphyrin-fullerene dyads.





Scheme 1. Synthetic target: the library of photoactive porphyrin-fullerene dyads 1.

2. Results and discussion

Taking into account the theoretical work of Buldum and our experimental results on the photocurrent induced by dyad **1aa**, we selected the co-axial orientation of the donor and acceptor fragments (tetraarylporphyrin and pyrrolofullerene respectively) to be the key structural parameter to be achieved in the synthesis of a photoactive donor-acceptor dyad. This can be implemented by constructing the pyrrolidine ring of the pyrrolofullerene fragment *via* 1,3-dipolar cycloaddition of suitable azomethine-ylides across [6,6]-double bond of fullerene C₆₀, which is known as Prato reaction.¹¹

Azomethine-ylides are usually highly reactive intermediates, which cannot be isolated in most cases and need to be generated *in situ*. In Prato reaction, azomethine-ylides are commonly generated by (i) condensation of α -amino acids with aldehydes or ketones¹²; (ii) prototropic isomerization of imines¹³ and (iii) electrocyclic ringopening of aziridines.¹⁴ Among these methods, the last approach suits best our synthetic goal. The potential advantages of the aziridine-based method for azomethine-ylide generation include stereospecificity of the ylide formation, the easy synthetic route towards the ylide precursor and the simplicity of introducing structural variations in the target dyads, as can be seen from the retrosynthetic disconnection of the target class of compounds down to commercial chemicals (Scheme 1).

The main synthetic problems to be solved for practical implementation of this route include the synthesis of unsymmetric A_3B -type porphyrin synthetic block, the construction of the aziridine ring bearing various alkoxycarbonyl groups and the verification of applicability of the synthesized set of porphyrinylaziridines in Prato reaction with fullerene C_{60} .

First, the variability of the alkoxycarbonyl groups in the key step of the dyad synthesis, in which the 1,3-cycloaddition of azomethine ylides across C=C bond of C_{60} , was tested on a model reaction series of fullerene C_{60} with dialkyl *N*-(*p*-methoxyphehyl)aziridine dicarboxylates **2**.

Aziridines **2** were obtained (Scheme 2) by condensation of *p*-methoxyaniline with alkylglyoxylate **3**, accessible by oxidative cleavage of dialkyl tartrates with periodic acid, followed by BF₃-catalyzed aziridination with alkyl diazoacetate **4**, accessible from

alkyl glycinate. The reaction proceeded smoothly for various combinations of alkyl substituents in the starting imine and the diazocompound yielding mixtures of *cis*- and *trans*-aziridines **2** in 79–99% yield (Table 1). In accord with the previous reports on aziridination reactions,¹⁵ *cis*-aziridines were the major products with the ratio of *cis/trans* aziridines in the range between 5:1 and 12:1.

Unsymmetrically substituted *trans*-aziridines *trans*-**2ab**, *trans*-**2ac** and *trans*-**2ad** showed expectable AB pattern at 3.44 ppm for the aziridine protons with ${}^{3}J_{\text{HH}}$ coupling constant of 2 Hz, typical for *trans*-aziridines.¹⁶ The corresponding AB signal for *cis*-aziridines *cis*-**2ab**, *cis*-**2ad** was reduced to a singlet shifted to the stronger field (3.0 ppm). Configuration of these aziridines and of symmetrically substituted aziridines **2aa**, **2bb**, **2 cc** and **2dd** was confirmed by observing the ${}^{3}J_{\text{HH}}$ coupling of the ${}^{13}\text{C}$ -satellite signals. *Cis*-aziridines are characterized by ${}^{3}J_{\text{HH}}$ of 6–7 Hz,¹⁷ while *trans*-aziridines show lesser value of 0–2 Hz (Table 1).

Aziridines **2** were reacted with fullerene C_{60} to give pyrrolofullerenes **5** (Scheme 2) in 25–59% yield (Table 2). The solubility of the resulting adducts increased dramatically when either one or both ethyl groups in **5aa** were changed for longer alkyl chains: *n*butyl, *n*-hexyl or *n*-octyl. The reaction of aziridines **2** with C_{60} proceeded stereospecifically, with *cis*-aziridines giving only *trans*adducts, and *trans*-aziridines – *cis*-adducts.

The configuration of the pyrrolofullerenes was established based on the chemical shift of the pyrrolidine $HC^{2(5)}$ proton in ¹H NMR spectra. The signal of this proton is shifted towards weak field for *trans*-pyrrolofullerenes as compared to *cis*-pyrrolofullerenes¹⁸ (6.5 and 5.7 ppm respectively). For unsymmetrically substituted pyrrolofullerenes **5ab**, **5ac** and **5ad**, the signals of the pair of non-equivalent pyrrolidine protons H² and H⁵ could be discerned as two singlets both for *cis*-isomers (5.69 and 5.71 ppm) and *trans*-isomers (6.50 and 6.51), except compound *trans*-**5ab**, where the corresponding signals coalesced into a single singlet (6.5 ppm) of double integral intensity. We attribute this to the strong deshielding effect of the carbonyl group in the case of *trans*-isomers, which masks the small differences in chemical surrounding of these protons. The non-equivalence of the CH fragments in the pyrrolidine ring can be seen in ¹³C NMR spectra of this pyrrolofullerene, where a pair of signals for C²⁽⁵⁾ carbons was observed (74.6 and

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