Wavelength-Gated Photochemical Synthesis of Phenalene Diimides

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Abstract: Herein, we pioneer a wavelength-gated synthesis route to phenalene diimides. Consecutive Diels–Alder reactions of methylsulfonfylaldehyde and maleimides afford hexahydro-phenalene-1,6-diol diimides via 5-formyl-hexahydrobenzof[f]isoindoles as the intermediate. Both photoreactions are efficient (82–99 % yield) and exhibit excellent diastereoselectivity (62–98 % d.r.). The wavelength-gated nature of the stepwise reaction enables the modular construction of phenalene diimide scaffolds by choice of substrate and wavelength. Importantly, this synthetic methodology opens a facile avenue to a new class of persistent phenalenyl diimide neutral radicals, constituting a versatile route to spin-active molecules.

Introduction

Polycyclic aromatic (di-)imides are a ubiquitous structural motif owing to the combination of an electron-rich aromatic system and a strong electron-withdrawing moiety.[I] These properties facilitate charge transport and have thus been exploited for a wide array of applications, such as organic light-emitting diodes,[II] organic field-effect transistors,[III] and organic photovoltaic devices.[IV]

Another important polycyclic aromatic hydrocarbon is the phenalenyl motif. Phenalenyl structures, in which three aryl rings share three C=C bonds, contain an uneven number of carbon atoms and, in the neutral state, possess an uneven number of electrons rendering them neutral radicals. Phenalenyls exhibit unique electronic properties and the remarkable ability to form stable anions, cations, and radicals through the redox chemistry of their non-bonding molecular orbital (NBMO).[V] The rigid and planar phenalenyl unit represents a delocalized neutral radical with the highest spin density in the α-position—analogous to a basic open-shell graphene fragment.[VI] For these reasons, the phenalenyl system is an important structural motif in organic spin chemistry[VI] with applications in organocatalysis,[VII] molecular conductors,[VIII] photovoltaics,[IX] and magnetic materials[X] and has been identified for use in synthetic quantum information devices.[XI] Organic molecules hosting persistent free radicals possess inherent spin-related properties that can be utilized for spin-active electronic devices.[XII] Common synthetic routes for phenalene derivatives proceed via phenalenones or 2,3-dihydrophenalenones as intermediates.[XIII] To our knowledge, no phenalenol decorated with diimide moieties has been reported.

In general, free radicals are reactive and therefore are difficult to generate, handle, and isolate. To be suitable for device applications, neutral radicals are required to be sufficiently stable to be processed and stored under ambient conditions. Primarily, two modifications can be exploited to improve the persistence of neutral free radicals in polycyclic aromatic systems, such as phenalenyls. First, electronic stabilization, by the introduction of heteroatoms, or second, kinetic stabilization, via spin delocalization and/or steric hindrance. Given most delocalized neutral radicals require multi-step syntheses and tedious workup procedures, simple tuning of the properties is not always feasible.

The synthesis of polycyclic aromatic diimides via Diels–Alder reaction of maleimides and light-generated orthoquinodimethanes (o-QDMs) was established by Meador et al.[XIV] involving multi-step synthesis of the precursors (5 to 7 steps), non-stoichiometric reagent ratios, harsh UV light, and limited reaction efficiency (49–81 % yield). Despite
the challenges, anthracene diimides, pyrene diimides, benzo-
pyrene diimides, and perylene diimides were obtained
(Scheme 1) and these reactions were later successfully
applied for the synthesis of polyimides.

In these pioneering studies, the authors hypothesized the potential for consecutive
formation of two equivalents of o-QDM, however successful step-wise trapping of the
o-QDMs with different maleimides was not reported. Unprecedented ability to
tune the diimide properties could be achieved with the
incorporation of two disparate diimide functionalities, how-
ever previous synthetic routes to heterobifunctional polycyclic aromatic diimides
required complex, multi-step syntheses.

The click-chemistry concept introduced by Kolb, Finn,
and Sharpless focusses on combining molecular building
blocks via highly efficient ligation reactions. The modular
nature of this approach has been demonstrated in many
studies, especially in the fields of bio[15] and polymer
chemistry.[16] The click concept can be further enhanced by
exploiting the spatio-temporal control of photochemical
reactions.[17] Already an indispensable tool in organic syn-
thesis,[18] photochemistry provides additional spatial and
temporal control over chemical transformations, enabling
the fabrication of nano-structured materials.[19] By exploiting the
energy contained in different wavelengths of light, distinct
reaction pathways can be accessed, affording the ability to
perform complex synthetic steps independently, which would
be difficult using conventional reaction conditions.[20]

We herein utilize the light-induced formation of highly
reactive dienes (o-QDMs) from dialdehydes and subsequent
Diels–Alder reaction with maleimide dienophiles to generate
phenalenyl diimide scaffolds. The activation of the two
carbonyl groups of a single chromophore in a consecutive,
wave-length-gated fashion represents the first example of such
a ligation system and allows for the modular assembly of
complex polycyclic molecules. The steric bulk of the imide
groups allows for the generation of persistent phenalenyl
diimide neutral radicals. Our concise approach eliminates the
barrier of complex synthetic procedures in organic spin
chemistry[6a] via the judicious design and tailoring of elec-
tronic spin structures.

Results and Discussion

Our synthetic strategy for phenalenyl diimide neutral
eradicals (PLYD) entails the generation of a fused ring system
via the stepwise, light-induced Diels–Alder reaction of
methylisophthalaldehydes (MIAs) and maleimides, followed
by an acid-catalyzed E1 elimination and oxidation (Scheme 1). There is currently no reported route to phena-
enyle derivatives via Diels–Alder reactions or hexahydro-
phenalene-1,6-diols. In addition, the generation of fused ring systems involving \( \alpha \)-QDMs in the formation of the bridgehead atom is rarely reported in the literature, however a few examples with modest yields do exist.\[iv\]

An efficient route to generate \( \alpha \)-QDMs is the photo-induced intramolecular hydrogen abstraction of a benzylic proton by an \( \alpha \)-formyl or benzoyl group.\[vii\] The photo-induced enolization of \( \alpha \)-methyl benzaldehydes (\( \alpha \)-MBAs) with a hydrogen bridge donor adjacent to the formyl group is known to allow for highly selective ligation reactions, even enabling the challenging synthesis of sequence-defined macromolecules.\[vii\] Herein, we combine these design principles in a single photoreactive 2-methylsophthalaldehyde entity. We demonstrate the wavelength-gated formation of \( \alpha \)-QDMs involving a single methyl group and trapping these highly reactive intermediates with maleimide.

Initially, the non-symmetric 2,5-dimethylsophthalaldehyde \( 1a \) was synthesized in two steps (55% overall yield, refer to Supporting Information Section II) via a Duff reaction and served herein as a model substrate for the photoreactions displayed in Figure 1. MIA \( 1a \) was irradiated in the presence of \( \alpha \)-ethyl maleimide \( 2a \) (2.20 equiv) with a 385 nm LED. 5-Formyl-hexahydro-benzof[\( j \)]isoindole (FBI) \( 3a \) was formed as the major product (Figure 1 A). Subsequent irradiation with a 365 nm LED led to the formation of hexahydro-phenalene-1,6-diol diimide \( 4a \), unexpectedly resulting in a blue fluorescence of the reaction mixture under UV irradiation (\( 4a \), \( \Phi_E = 15 \pm 2\% \), \( \Delta \text{max} = 450 \text{ nm} \)). 365 nm LED irradiation of a mixture of \( 1a \) and \( 2a \) (2.20 equiv) affords \( 4a \) directly. Further experiments utilizing a tunable laser as monochromatic light source, revealed the wavelength-gated nature of the photoreaction (for details refer to Supporting Information Section IV). Reaction solutions consisting of \( 1a \) and \( 2a \) (2.20 equiv) were irradiated with an identical number of photons with wavelengths varying from 300 nm to 415 nm and the conversion to the monoadduct \( 3a \) and diadduct \( 4a \) was determined by \( ^1 \)H NMR spectroscopy. For comparison of the respective conversions with the UV/Vis absorbance spectra of the chromophores refer to Figure 1 B. At longer wavelengths (> 385 nm), the addition of one equivalent of \( \alpha \)-ethyl maleimide afforded the cycloadduct \( 3a \) exclusively. As the photon energy increases, the addition of a second equivalent of \( \alpha \)-ethyl maleimide can be observed below 375 nm and eventually the cycloadduct \( 4a \) becomes the dominant product in the reaction solution below 340 nm. To quantify this observation the reaction quantum yields for the first addition at 385 nm (\( \Phi_{385\text{nm}} = 38 \pm 7\% \), and for the second addition at 350 nm (\( \Phi_{350\text{nm}} = 8.8 \pm 1.2\% \) ) were determined (for details refer to Supporting Information Section IV), underpinning the wavelength-dependency of the observed conversions. As a result, the reaction selectivity to form either monoadduct \( 3a \) or double adduct \( 4a \) can simply be controlled by the choice of wavelength. For example, by reducing the equivalence of maleimide to 1.02 equiv, and irradiating with 385 nm, the product \( 3a \) can be formed exclusively (> 99% yield of isolated product). In a situation with no wavelength selectivity, a 1:2:1 mixture of \( 1a \), \( 3a \), and \( 4a \) would be the expected outcome of this experiment. The wavelength-selective nature of the two consecutive reactions is, in part, attributed to a 20 nm hypsochromic shift of the n–\( \pi^* \) absorption band of \( 3a \) compared to \( 1a \).

With the ability to now introduce two disparate imide functionalities in a simple synthetic methodology, the mechanism, and scope within which this reaction can be applied, was investigated. While various electron-deficient dienophiles should participate in these cycloadditions, symmetrical

![Figure 1](https://example.com/fig1.png)

Figure 1. A) \( ^1 \)H NMR spectra and assigned resonances of the reaction between MIA \( 1a \) and maleimide \( 2a \) affording cycloadduct \( 3a \) under irradiation with a 385 nm LED and subsequently to form cycloadduct \( 4a \) under irradiation with a 365 nm LED (LED-emission spectra Supporting Information Figure S1). The NMR spectra were recorded after removing the solvent from the respective batch photoreactions without further purification (excess \( \alpha \)-ethylmaleimide is removed in vacuo). For detailed characterization data (\( ^{13} \)C, 2D-NMR spectra, and LC–HRMS) of all compounds as well as experimental details refer to the Supporting Information Figures S20, S21, S27, S28, S36–S40, S90, S96 and Supporting Information Section VI. B) Molar extinction coefficients of \( 1a \) (solid black), \( 3a \) (dashed blue) and \( 4a \) (dash–dot brown) overlaid with the wavelength-dependent reactivity of the substrate \( 1a \) (1.6 mmol L\(^{-1} \) of \( 1a \) with 2.20 equiv of \( 2a \) in CD3CN) after irradiation with (9.4 ± 0.2) × 10\(^{14} \) photons of each wavelength from a 20 Hz, 7 ns tunable OPO laser. The conversions are determined by \( ^1 \)H NMR spectroscopy (Supporting Information Figures S87 and S88).
maleimides were chosen in order to limit the diastereomeric complexity. An overview of these results is shown in Figure 2.

In Supporting Information Sections II and III the synthetic details are elaborated. For the synthesis of the FBIs, MIA $1a$ and $1.02$ equiv of the respective maleimide ($2a$–$2c$) were irradiated with a 385 nm LED. To convert the FBIs to hexahydrophenalene-1,6-diol diimides (HPDDs) another $1.20$ equiv of the respective maleimide was added and the mixture irradiated with a 365 nm LED. For the HPDDs consisting of two similar maleimides ($4a$, $4c$, $4f$), the MIA $1a$ and $2.25$ equiv of the respective maleimide were irradiated with a 365 nm LED. An additional symmetric MIA $1b$ was synthesized via Duff reaction. The photoreaction of $1b$ with maleimide $2c$ was then conducted under irradiation with a 385 nm LED to afford $4g$ in excellent yield (99%).

As mentioned above, through the choice of symmetrical maleimides the number of possible diastereomeric products is limited. Even still, the HPDDs $4a$–$4g$ all feature seven adjacent stereocentres, formed by the two consecutive Diels–Alder reactions. The trajectory for the second maleimide addition can potentially lead to both syn- or anti-products (Figure 2D).

Furthermore endo- and exo-addition can occur for both maleimide additions. All the aforementioned reaction pathways combined would lead to a mixture of various diastereomers. For a more detailed discussion of the stereochemistry and a collation of all relevant transition states and diastereo-

Figure 2. A) Proposed mechanism of the light-induced (Z)-enol formation of MIA $1a$, transition state of the subsequent Diels–Alder reaction with maleimides forming endo-FBIs and light-induced (E)-enol formation of FBIs, transition state of subsequent Diels–Alder reaction with second maleimide resulting in the formation of endo/endo-HPDDs. B) Not observed FBI regioisomers by initial enolization of the p-formyl instead of the o-formyl moiety. C) Exo-addition to MIA forming exo-FBI and subsequent anti-endo addition. This reaction sequence is realized in HPDD exo-4b. D) Observed anti-exo addition transition state forming the endo/exo diastereomer, realized in exo-4e and not observed syn-endo addition from the sterically disfavoured trajectory. E) Influence of the non-planarity of maleimide substrate $2c$ on the endo/exo selectivity of the Diels–Alder reaction. F) Substrates: MIA $1a$, $1b$ and maleimides $2a$–$2d$. G) Isolated FBIs $3a$, endo/exo-3b, and $3c$. H) Isolated HPDDs 4a–4g. Triclinic crystal structure (ellipsoids with 50% probability) of HPDD $4a$, displayed as pair of enantiomers within the asymmetric unit. Stereocentres in the molecules depicted in (C–H) represent one enantiomer of the obtained racemic mixture. 1 Yield of isolated product after diastereomer separation. 2 Yield of isolated product from two separate reactions (substances endo-3b and exo-3b).
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A recent theoretical study of different phenalenyl radicals revealed that the best thermodynamic stabilization is provided by either \( p \)-conjugated or lone-pair substituents with low electronegativity, for instance \(-\text{CN}\) or \(-\text{NH}_2\), respectively, when attached to a \( \alpha \)-position.\(^{32}\) \( 6a \) represents the first example where the stabilization of a phenalene radical is provided by pendant imide or maleimide groups. We hypothesize that a push–pull effect of the \( \alpha \)-OMe and the \( \alpha \)-imine units of the two maleimides provides additional stabilization. To confirm this, three additional PLYD radicals were synthesized from HPDDs using an identical procedure (refer to Supporting Information Section VII; g-factors and hffcs are summarized in Table S2). By introducing electron-withdrawing aryl groups on the maleimides and an additional OMe group in the \( \alpha \)2 position, a PLYD radical derived from \( 4g \) was obtained which possessed increased stability at ambient conditions for several weeks allowing for additional LCMS and cyclic voltammetry analysis (refer to Supporting Information Section VII). Also, a heterobifunctional PLYD radical derived from \( 4d \) could be easily obtained. An additional systematic study of the structure–property relationship of the herein presented phenalenyl diimide neutral radicals and detailed DFT calculations of the molecular orbitals are envisaged for the future.

**Conclusion**

The methodology presented herein combines the high efficiency of click chemistry with the spatiotemporal control of light-induced reactions, enabling the wavelength-gated generation of heterobifunctional phenalene diimides. The wavelength dependency of the two consecutive \( \text{ortho} \)-quinodimethanes was studied in detail employing a monochromatic light source. The diastereoselectivity of the cycloadditions was investigated by combining planar and non-planar maleimide substrates and independently confirmed via single-crystal XRD. The approach represents the first wavelength-selective bond forming of a single chromophore and holds key potential for the light-driven assembly of complex architectures.

Subsequent transformation of the phenalene diimides to a new class of persistent neutral radicals (PLYDs) was established and the produced spin-active molecules were studied. Our approach thus greatly simplifies the synthetic procedures in organic spin chemistry and allows for the design of tailor-made electronic spin structures.

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**Conflict of interest**

The authors declare no conflict of interest.
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