

Cyanated Perylene-3,4-dicarboximides and Perylene-3,4:9,10-bis(dicarboximide): Facile Chromophoric Oxidants for Organic Photonics and Electronics

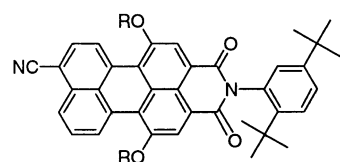
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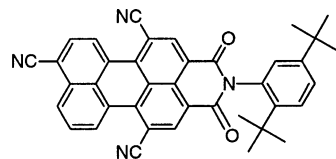
Received March 10, 2003
Revised Manuscript Received May 8, 2003

The development of organic photonics and electronics has fueled the need for stable chromophores that can undergo photoinduced electron-transfer reactions to yield stable radical ion intermediates. Derivatives of perylene-3,4:9,10-bis(dicarboximide) (PDI) and perylene-3,4-dicarboximide (PMI) are especially intriguing because they show exceptional chemical and photochemical stability.¹ These molecules and their derivatives have been used as building blocks for molecular switches, wires, and logic gates,^{2–4} as well as organic light-emitting diodes,^{5,6} light-harvesting arrays,^{7,8} photorefractive thin films,^{9,10} and solar cells.^{11,12} Much of this work has benefited greatly from the distinct electronic absorption spectra that the radical ions of these molecules exhibit,¹³ and their ability to self-assemble into extended structures.^{14–16} The former makes it possible to easily identify these radical ion intermediates in complex electron-transfer reactions, while the latter offers the possibility of self-assembling photofunctional

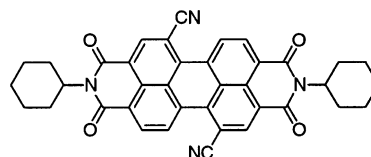
materials. The photophysical and redox properties of these molecules can be manipulated by functionalizing the perylene core with electron-donating and -accepting functional groups. For example, substitution of the 1,7-positions of PDI or the 9-position of PMI with *N*-cycloalkylamines, such as *N*-pyrrolidine, produces chromophores in which the lowest energy electronic transition acquires significant charge-transfer character and moves to substantially longer wavelengths relative to those of PMI or PDI.^{17,18} Moreover, the one-electron oxidation potentials become significantly less positive, making these derivatives excellent electron donors in donor–acceptor materials.¹⁹ We report here the preparation and properties of the cyanated chromophores CN₂PDI, CN₃PMI, and CN₃PMI and their electrochemically generated radical anions. These molecules are designed to serve as stable, photochemical oxidants for use in novel photonic and electronic materials.



CNPMI R = 3,5-di-*tert*-butylphenyl



CN₃PMI



CN₂PDI

The immediate precursors to the cyanoperylene are the corresponding bromo derivatives: *N,N*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-bis(dicarboximide),²⁰ *N*-(2,5-*tert*-butylphenyl)-9-bromoperylene-3,4-dicarboximide, and *N*-(2,5-*tert*-butylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide,²¹ which are readily synthesized in high yields by direct bromination of the parent hydrocarbons. Classical cyanation procedures using CuCN in refluxing DMF failed to produce the desired cyano compounds. In all three cases this procedure resulted in significant yields of debrominated products. Recently, Zn(CN)₂ or CuCN in the presence of a Pd(0) catalyst has been used

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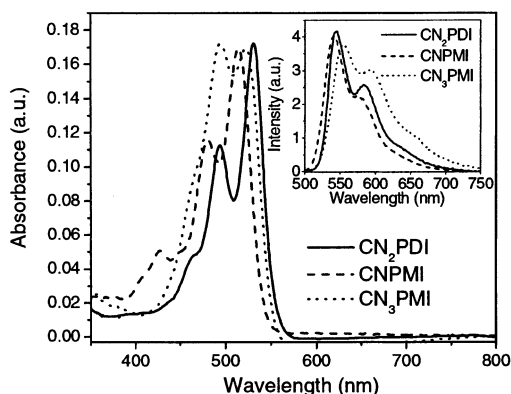


Figure 1. Electronic absorption and fluorescence (inset) spectra of the indicated compounds in toluene. Fluorescence spectra were obtained following excitation at 480–490 nm.

Table 1. Photophysical and Electrochemical Properties

compd	λ_{abs} (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	λ_{em} (nm)	E_{S} (eV)	φ_{F}	$E^{-1/2}$ (V)	$E^{2-1/2}$ (V)
CN ₂ PDI	530	47000	545	2.30	1.0	-0.07 ^a	-0.40 ^a
CNPMI	515	61000	541	2.35	0.91	-0.73 ^b	-1.14 ^b
CN ₃ PMI	522	60000	554	2.30	0.83	-0.19 ^a	-0.72 ^a

^a Butyronitrile + 0.1 M Bu₄NClO₄. ^b Butyronitrile + 0.1 M Bu₄NPF₆. Electrochemical potentials vs SCE absorption spectroscopy, even when they are in the presence of other perylene derivatives.

to convert bromoarenes into cyanoarenes in excellent yields.^{22,23} We used the Zn(CN)₂ method to quantitatively convert all three bromoperylene derivatives to the corresponding cyano compounds, as detailed in the Supporting Information.

The ground-state absorption and emission spectra of the neutral molecules in toluene are shown in Figure 1. The intense absorbance maxima for each of these chromophores are near 500 nm and are only slightly shifted in wavelength relative to those of unsubstituted PMI (512 nm) and PDI (526 nm).¹³ In addition to the usual vibronic progression present in each of these rigid aromatic molecules, the spectrum of CNPMI shows an additional band at 420 nm, which is typical of 1,6-bisphenoxyated PMI derivatives. The 420-nm band partially obscures the second vibronic band of CNPMI at 450 nm. The cyanated derivatives all fluoresce with quantum yields $\varphi_{\text{F}} > 0.8$, determined relative to rhodamine 640 (Table 1). The absorption and emission features of these molecules are not solvatochromic, which coupled with the high fluorescence quantum yields suggest that their lowest excited singlet states possess little or no charge-transfer character. The energies of the lowest excited singlet states, E_{S} , were estimated by averaging the energies of their absorption and emission maxima, λ_{abs} and λ_{em} , respectively.

Cyclic voltammetry on the cyanated derivatives shows that the one-electron reduction potentials ($E^{-1/2}$ and $E^{2-1/2}$) of each molecule are more positive than those of the unsubstituted analogues (PMI: $E^{-1/2} = -0.96$, $E^{2-1/2}$

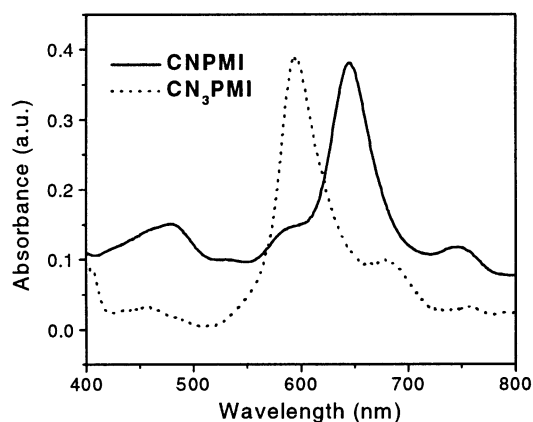


Figure 2. Electronic absorption spectra of CNPMI and CN₃PMI in butyronitrile containing 0.1 M Bu₄NPF₆ and 0.1 M Bu₄NClO₄, respectively, following controlled potential electrolysis at -0.9 and -0.3 V vs SCE, respectively.

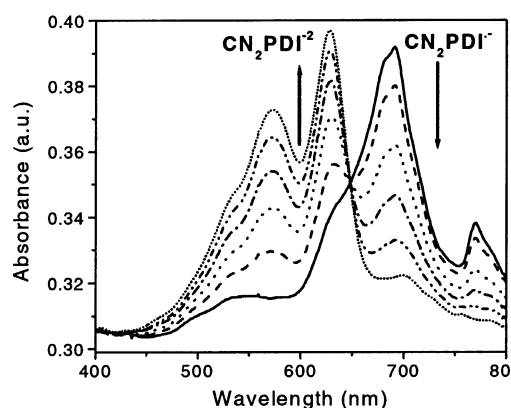


Figure 3. Electronic absorption spectra of CN₂PDI⁻ and CN₂PDI²⁻ in DMF containing 0.1 M Bu₄NClO₄ following controlled potential electrolysis at -0.1 V vs SCE and at -0.6 V vs SCE, respectively.

$= -1.55$ V; PDI: $E^{-1/2} = -0.43$ V, $E^{2-1/2} = -0.70$ V, all vs SCE)¹³ (Table 1). CN₂PDI and CN₃PMI show exceptionally large positive shifts in redox potential. Spectroelectrochemical measurements yield the electronic absorption spectra of the radical anions of CNPMI, CN₃PMI, and CN₂PDI and the dianion of CN₂PDI.

The electronic absorption spectra of CNPMI⁻ and CN₃PMI⁻ in butyronitrile (Figure 2) show that the absorption characteristics of the neutral molecules are replaced by new bands in the visible spectrum upon reversible electrochemical reduction of the chromophore to its radical anion. For example, the spectrum of CNPMI⁻ is characterized by an intense absorption band at 644 nm, with minor bands at 480 and 735 nm. The spectrum of CN₃PMI⁻ is similar to that of CNPMI⁻ with an intense band at 595 nm and weaker bands at 458 and 680 nm. These bands can be compared to the corresponding intense absorption of PMI⁻ at 588 nm. Figure 3 shows the spectra of CN₂PDI⁻ and CN₂PDI²⁻ obtained by controlled potential electrolysis of CN₂PDI, first at -0.1 V vs SCE and then at -0.6 V vs SCE. At the more negative potential, CN₂PDI⁻ is cleanly and reversibly converted to CN₂PDI²⁻ as noted by the isosbestic point at 650 nm. The intense absorption band of CN₂PDI⁻ at 691 nm is blue-shifted relative to that of PDI⁻ at 712 nm, while the corresponding absorption band of CN₂PDI²⁻ at 628 nm is red-shifted relative to

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that of PDI²⁻ at 570 nm.¹³ The relatively sharp bandwidth of these absorption features should make it possible to readily identify the presence of these radical anions and dianions as intermediates in electron-transfer reactions using transient absorption spectroscopy, even when they are in the presence of other perylene derivatives.

To demonstrate the effectiveness of CN₂PDI as a strong oxidant, we monitored the spectrum of this compound in the presence of an oxidizable species. For example, a 10⁻⁵ M solution of CN₂PDI in dry DMF shows an absorption feature at 691 nm, indicating that about 15% of CN₂PDI is converted to CN₂PDI^{·-} under ambient oxygenated conditions. Bubbling dry N₂ through the solution for 15 min produces a dramatic increase in the intensity of the CN₂PDI^{·-} spectrum, indicating about 60% conversion to the radical anion (see Supporting Information). Since DMF typically contains a small amount of *N,N*-dimethylamine due to decomposition, we reason that CN₂PDI oxidizes the amine. The aminium radical cation decomposes rapidly, yielding a proton, which is the counterion for the stable CN₂PDI^{·-}. This same effect can be observed in toluene, which is not oxidized by CN₂PDI, by adding a small amount of triethylamine to the toluene solution. While the first reduction potential of CN₂PDI is very similar to the well-known oxidant, chloranil ($E[A/A^-] = 0.02$ V vs SCE),²⁴ the radical anion and dianion of CN₂PDI, unlike the reduced chloranil species, are excellent chro-

mophores themselves and are not susceptible to decomposition through irreversible protonation reactions. Moreover, both CN₂PDI and CN₃PMI are significantly easier to reduce than C₆₀ ($E[A/A^-] = -0.38$ V vs SCE),²⁵ which is a typical electron acceptor in organic materials.

The availability of these strong perylene-based oxidants expands the library of perylene derivatives that can be employed as stable charge generators and carriers in molecular photonics and electronics applications. We are currently investigating the ability of these molecules to engage in photoinduced electron-transfer reactions in both covalent and self-assembled structures as well as to serve as the basis for new n-type organic semiconductors.

Acknowledgment. The authors wish to thank Dr. Alexey Gusev for assisting with spectroelectrochemistry measurements. This work was supported by the Office of Naval Research.

Supporting Information Available: Synthetic and spectroscopic details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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