



Fluorinated perylene diimides: synthesis, electrochemical–photophysical properties, and cellular imaging



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ABSTRACT

We report the synthesis and properties of perylene diimides with fluorinated substituents on the bay (**BFPDIs**). These **BFPDIs** exhibit good water solubility, high extinction coefficients, and high fluorescence quantum yields. Furthermore, these **BFPDIs** are used as probes in cellular imaging.

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Introduction

Perylene diimides (**PDIs**) represent a class of organic chromophores with photochemical stabilities, high extinction coefficients, and high quantum yields.^{1,2} **PDIs** are key chromophores for high-tech applications, such as organic photovoltaics,³ organic field-effect transistors,⁴ biolabeling,⁵ sensors,⁶ single molecular spectroscopy,⁷ and supramolecular assemblies.⁸ Stability, chemical robustness, and ease of preparation are among a few of the necessary characteristics for organic chromophores used in these fields.⁹ Currently available synthetic methods allow the preparation of stable chromophores with increasingly negative reduction potentials.¹⁰

Fluorine is the strongest element with electron affinity and a small atom that can be introduced onto molecules with minimal effect on steric hindrance. Highly fluorinated materials display a variety of interesting properties, such as thermal and chemical stability, low surface energy, and high resistance to oxidation.¹¹ Swager and co-workers have recently reported two highly fluorinated poly(*p*-phenylene ethynylene)s with outstanding fluorescence quantum yields in solution and in thin films.¹² Furthermore, fluorinated polymers are also biocompatible. Zhang et al. reported a highly fluorescent fluorinated semiconducting polymer dot that is eight times brighter in cell-labeling applica-

tions than its non-fluorinated counterpart.¹³ These successful applications point to the potential of fluorinated chromophores in biological applications.

Our group aims to develop photochemically stable and biocompatible perylene dyes with high fluorescence in aqueous solutions for bioimaging.¹⁴ In this study, we report the synthesis of perylene diimides with fluorinated substituents on the bay (**BFPDIs**), as well as their electrochemical–photophysical properties and applications for cellular imaging.

Results and discussion

Chart 1 shows the chemical structures of **BPPDI** and **BFPDIs**, which were efficiently synthesized by the stepwise synthetic protocol illustrated in **Scheme S1**. **BPPDI** without fluorinated substituents on the bay was used as a reference compound to study the mechanisms by which fluorinated substituents affect the properties of **PDIs**. Dibromo-perylene tetracarboxylic dianhydride¹⁵ and 2,5,8,12,15,18-hexaoxa-10-nonadecanamine¹⁶ were prepared according to the literature procedures. The reaction of 2,5,8,12,15,18-hexaoxa-10-nonadecanamine **1** with Cbz-protected L-aspartic acid yielded compound **2**. The Cbz group was removed by catalytic hydrogenation with Pd/C to obtain compound **3**. Compound **5** was obtained via a coupling reaction between dibromoperylene tetracarboxylic dianhydride and compound **3**. **BPPDI** and **BFPDIs** compounds were prepared by Suzuki coupling with compound **5** and the corresponding phenylboronic acid, followed

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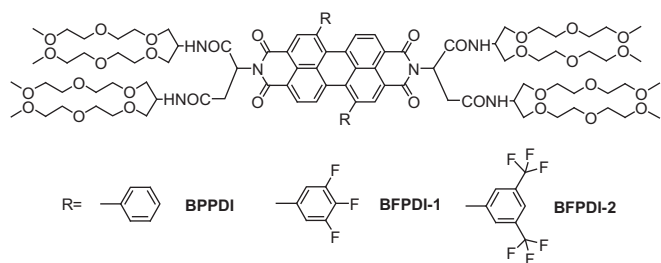


Chart 1. Chemical structures of BPPDI and BFPDIs.

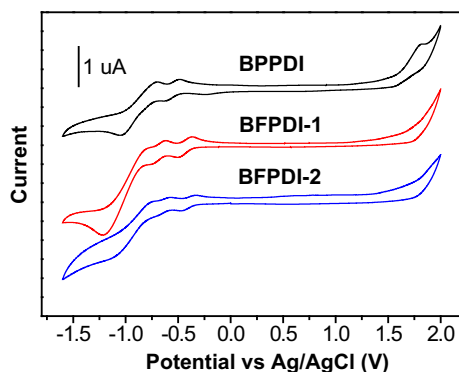


Figure 1. Cyclic voltammograms of compounds BPPDI and BFPDIs in dichloromethane at a scan rate of 0.1 V/s.

by purification through column chromatography on silica gel. These new perylene diimides were fully characterized by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy and matrix-assisted

laser desorption/ionization mass spectrometry (MALDI-TOF-MS). Details of the synthetic route and all spectroscopies are provided in the [Supporting information](#).

The electrochemical properties of BPPDI and BFPDIs in dichloromethane were studied in a three-electrode electrochemical cell using Bu_4NPF_6 (0.1 M) and Ag/AgCl as the electrolyte and the reference electrode, respectively. The CV curves are shown in [Figure 1](#). BPPDI revealed one irreversible oxidation potential at 1.69 V versus Ag/AgCl and one reversible reduction potential at -0.55 V versus Ag/AgCl. After installing the fluorinated substituents on the bay of PDIs, the first reduction potentials of BFPDIs (-0.40 V for BFPDI-1, -0.38 V for BFPDI-2) were shifted by approximately 150 mV toward more positive potentials compared with that of BPPDI. These BFPDIs showed an increase in the first reduction potential, indicating that the electron-accepting power increased in strength. By contrast, the CV scan for the BFPDIs with anodic scanning from 0 to 2 V showed no peaks, suggesting that the electron-donating property of the BFPDIs became weak. The lowest unoccupied molecular orbital (LUMO) levels were estimated from the onset of the first reduction potentials.¹⁷ LUMO levels of the three compounds were calculated as -3.85 eV, -4.00 eV, and -4.02 eV, respectively. The decreased LUMO levels are ascribed to the electron-deficient fluorinated substituents on the bay of perylene diimides.

The optical properties of BPPDI and BFPDIs in water were studied and compared with those in toluene. In the hydrophobic toluene solvent, the absorption maximum of BPPDI appeared at 551 nm, along with higher vibronic transitions located at 518 nm ([Fig. 2A](#)). With fluorinated benzene on the bay, the maximum absorption of the BFPDIs was blue-shifted to 542 nm for BFPDI-1 and 539 nm for BFPDI-2. Interestingly, the extinction coefficients of these fluorinated PDIs were higher than that of the non-fluorinated counterpart. The photoluminescence (PL) peak of BPPDI in toluene solution appeared at 606 nm. With fluorinated substitu-

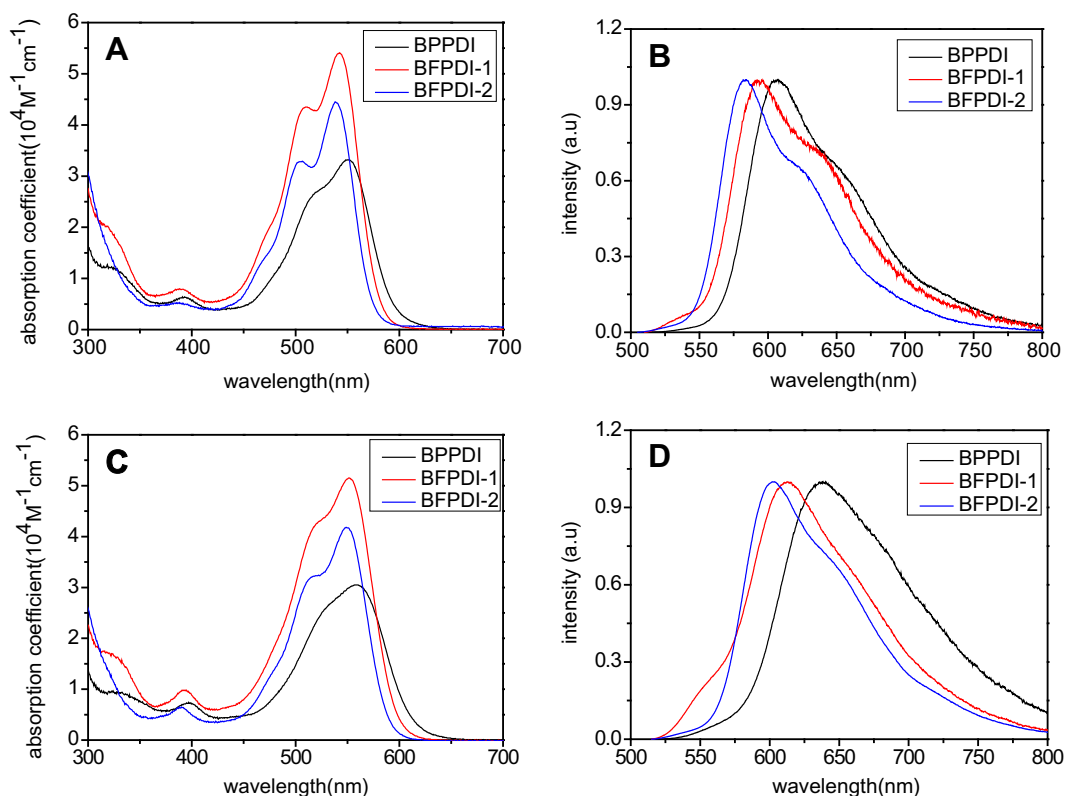


Figure 2. UV-vis absorption at 1.0×10^{-4} M and PL spectroscopy at 1.0×10^{-5} M of PDIs in toluene solution (A, B) and aqueous solution (C, D).

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