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Fulvalene Embedded Perylene Diimide and Its Stable Radical Anion

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Abstract: Reported herein is the first example of a two-state (neutral and reduced), stable electron-accepting material and its radical anion. FV-PDI, generated from cyclocarbonylation and then a carboxyl coupling reaction, shows a largely degenerated LUMO level of -4.38 eV based on the delocalization of π-electrons across the whole molecular skeleton through a fulvalene bridge. The sufficient stability and electron affinity allow spontaneous electron transfer to afford a stable radical anion. Full spectroscopic characterization and structural elucidation showed that the radical anion [FV-PDI]⁻ has remarkable stability and near-infrared absorptions extending to 1200 nm. Single-crystal X-ray diffraction analyses revealed significant changes in the molecular shape and packing arrangement of the formed radical anion. More importantly, the central C-C bond linking the two PDI halves is lengthened from approximately 1.33 to 1.43 Å, and the alternating arrangement of positively and negatively charged units are favor the stable charge-transfer complex.

Organic radicals and radical ions with appreciable stability have attracted increasing attention due to their practical applications in molecular magnetism, in organic spintronics, and as biological probes.1 In recent years, there has been ongoing interest in the development of radicals and radical ions with fascinating optoelectronic properties.2 In fact, the intrinsic high reactivity of radical species and their susceptibility to reoxidation by air is ubiquitous. One of the most notable strategies for accessing these systems is to use extremely electron-deficient π-systems as precursors, thus endowing the final product with higher electron affinity for spontaneously capturing electrons to form stable organic radicals.3 A growing number of highly electron-deficient precursors with lower LUMO levels were reported.4 However, the rational design of a system in which the electron deficiency and stability are balanced, allowing the construction of a two-state (neutral and reduced) stable electron-accepting material, remains very challenging.

Perylene diimides (PDIs) are among the most important and useful electron-deficient π architectures, and they have attracted ever-increasing academic attention owing to their simple functionalization and excellent optoelectronic properties.5 The impressive performances of PDIs as electron acceptors in optoelectronics, such as organic field-effect transistors (OFETs)6 and solar cells (OSCs),7 highlight their facile chemical, electrochemical, and photochemical reduction from neutral PDIs to anionic species by the in situ extracting of electrons and transporting charge carriers. Additionally, the PDI-based radical anions (PDI⁻) featuring a significantly redshifted absorption to the near-infrared region (NIR) are generally promising for photothermal therapies.8 Nevertheless, the stability of PDI⁻ species remains a scientific challenge, and only very recently have experimental examples of core-modified PDI⁻ and in situ-formed PDI⁻ species for films, supramolecular assemblies and metal-organic frameworks (MOFs) been reported.9,10,11

Figure 1. The design of electron-deficient fulvalene embedded perylene diimide (FV-PDI).

Fulvalene features two five-membered rings linked by a double bond, and each five-membered ring is prone to accepting one electron to relieve the steric strain and become aromatic.10 The parent form is very unstable, and to date, there have been a large number of derivatization studies focused on addressing the stability and functionalization of fulvalenes by traditional substitution reactions, aryl annihilations, or coordination with transition metals.11 To the best of our knowledge, a fulvalene derivative fused with an electron-deficient skeleton has not yet been reported. Herein, we designed and synthesized a fulvalene embedded perylene diimide (FV-PDI), the first example of a dichromophoric PDI structure, by integrating a fulvalene fused between two PDI halves. Consequently, FV-PDI showed a largely degenerated LUMO level of -4.38 eV due to the delocalization of the π-electrons across the whole molecular skeleton through the fulvalene bridge. The low-lying LUMO provides sufficient stability and electron affinity, making this a good candidate as an electron-accepting material.

Scheme 1 illustrates the synthesis of FV-PDI. Cyclocarbonylation is an important process for producing cyclopentadionene derivatives, but this reaction is essentially limited to electron-rich systems such as benzenes, thiophenes, pyrroles and their derivatives according to previous accounts.12 In our strategy, the cyclopentadionene-annulated PDI (2) in the

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bay regions was readily prepared by cyclocarbonylation from Br-PDI (1) as the starting material using Mo(CO)₅ as the carbonyl reagent, as can release carbon monoxide in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with heating in toluene. This is the first example of the cyclocarbonylation of an electron-deficient system, greatly extending the derivatization of PDIs. Furthermore, intermediate 2 can be decarbonylated to afford compound 5 in a very high yield of 90% under H₂PO₄/H₂O in refluxing HOAc for 1 h, which is exciting because it is quite challenging to construct systems with five-membered carbon rings fused onto the bay regions of PDI. With the key precursor in hand, we succeeded in synthesizing FV-PDI (3) based on the carbonyl coupling reaction of 2 with Woollins’ reagent. As shown in Scheme 1, FV-PDI, in which two PDIs are fused onto a fulvalene coupled with a double bond, was produced as a red solid in a high yield (75%) under the optimized reaction conditions. This two-step reaction toward a multichromophoric PDI architecture provides a new platform for accessing novel PDIs and electromagnetic studies of PDI-fused systems.

![Scheme 1. Synthetic route to FV-PDI (3) and its radical anion [FV-PDI]⁻ (4).](image)

To illuminate the electron-accepting properties of FV-PDI, we first conducted cyclic voltammetry (CV) measurements in a CHCl₃ solution using ferrocene as an internal potential marker. As illustrated in Figure 2a, FV-PDI featured two one-electron and one two-electron reductive waves within the accessible scanning range, and these waves indicated full conjugation across the whole π-skeleton. The three half-wave reduction potentials vs Fc/Fc⁺ are estimated to be -0.56, -0.68, and -1.64 V. Relative to that of the parent PDI (E₁/₂ = -1.10 V), the first half-wave reduction potential is much less negative, indicating that the imbedded electron-deficient fulvalene moiety results in a much higher electron affinity. Therefore, this fusion causes FV-PDI to have a lower LUMO level of -4.38 eV, giving it sufficient stability and electron affinity to make it an ideal electron acceptor.

We then investigated the electron transfer (ET) properties of FV-PDI with cobaltocene (CoCp₂), which tends to lose an electron, yielding a stable, 18-electron cobaltocene. The first ionization energy (IE) of CoCp₂ is -4.07 eV, which is higher than the LUMO of FV-PDI, meaning that spontaneous ET will occur from CoCp₂ to FV-PDI under certain conditions (Figure 2b). Upon mixing the two components in CHCl₃ at room temperature under argon, a color change from red to purple will occur within seconds, and the layering of hexane onto this solution resulted in the formation of a black-purple crystalline precipitate. As expected, the isolated precipitate, identified as radical anion [FV-PDI]⁻ (4), is highly stable even upon exposure to air without any protection, allowing complete spectroscopic characterization as well as single-crystal structural analysis. Figure 2a shows the CV behavior of [FV-PDI]⁻, and the voltammogram possessed four reductive peaks with slight positive shifts relative to its neutral state. The reduction properties of this resulting radical anion included characteristics of both FV-PDI and CoCp₂ with a LUMO level of -4.41 eV.

![Figure 2. (a) Cyclic voltammograms in deaerated CHCl₃ solution containing Bu₄NPF₆ (0.1 M) and FV-PDI (dark cyan trace), [FV-PDI]⁻ (purple trace), and CoCp₂ (black trace), (b) Energy levels of FV-PDI and CoCp₂ and a schematic of the intermolecular electron transfer process.](image)

The UV-vis-NIR absorption spectra of FV-PDI and [FV-PDI]⁻ in chloroform are shown in Figure 3a and indicated the presence of certain structural features. FV-PDI displayed a broad, weak peak from 550 to 900 nm, which was attributed to intramolecular charge transfer (ICT), and this was further supported by the spectra calculated using time-dependent density functional theory (TDDFT). As shown in Figure S2, the lowest energy band from 650-900 nm arising from the S₀-S₁ transition primarily involved a HOMO→LUMO transition. This electron transition dominates 94.1% of the excited state. From the energy orbital distribution, the HOMO is mainly distributed on the perylene core, while the LUMO is mainly distributed on the fulvalene, suggesting that a weak ICT process could occur from the PDI to the fulvalene portion. Additionally, the higher energy absorption peak at 493 nm was attributed to local excitation from the perylene core (S₀-S₂) and was blue-shifted relative to that of PDI (λmax = 527 nm). The other sharp peak at approximately 529 nm was assigned to local excitation from the fulvalene unit (S₀-S₃). All the calculated spectra are in good agreement with the experimental results. Unlike the less disturbing electrochemical properties, the absorption of [FV-PDI]⁻ was significantly re-
shifted and showed sharp bands at approximately 518 and 639 nm. Moreover, a new broad and strong peak from 700 nm to 1200 nm, characteristic of a delocalized radical anion, was observed. The optical energy gaps in the CHCl₃ solutions are estimated to be 1.39 eV for FV-PDI and 1.05 eV for [FV-PDI]^-. Of the solution exposed to air for 1 h while shielded from light at 298 K (shown in the inset) is almost unchanged. The test was performed over a one-week period, and no significant variations were observed in the spectra, indicating extraordinary stability of this compound toward ambient conditions.

The infrared (IR) spectra of FV-PDI and [FV-PDI]^− were acquired to elucidate the radical anion interactions (Figure S4). After carefully examining the IR spectra, the characteristic peaks of the C=O groups of FV-PDI at 1700 cm⁻¹ and 1661 cm⁻¹ were shifted to lower frequencies of 1665 cm⁻¹ and 1626 cm⁻¹ in the spectrum of [FV-PDI]^−. According to Hook’s Law, these spectral changes can be attributed to the increased electron density on the PDI core as the increase in electrons decreases the force constant (K). Electron spin resonance (ESR), shown in Figure 4, was performed to provide evidence for unpaired electrons in this system. From the spectra, one intense resonance with a g-factor of 2.00376 was observed at room temperature, indicating the existence of unpaired electrons in the generated ET complex. The calculated spin density plot of a simplified model system indicated that the single electron was delocalized over the whole PDI skeleton, especially the fulvalene unit (C1-C5). Almost all the C atoms in the PDI core show a positive spin, except C6-C9, which have a small residual negative spin. This result supported that the resonance has no hyperfine splitting with the carbon or nitrogen nuclei of the aromatic core, making it less informative.

The absorption spectra of mixtures of FV-PDI and CoCp₂ at different ratios were acquired to explore the stoichiometry of ET complex formation (Figure S5). The absorption spectrum changes significantly, and the main peaks of FV-PDI at approximately 450 to 550 nm are red-shifted by the gradual addition of CoCp₂. When the mixing ratio of FV-PDI and CoCp₂ reached 1:2, a new absorption band is formed, which is consistent with the measured absorption spectra of the ET complex. This is mainly caused by the formation of radical anion [FV-PDI]^−, which was further confirmed by single-crystal XRD analysis. The absorption bands become stable when the concentration of CoCp₂ was further increased, meaning that the saturated stoichiometric ratio was needed for the ET process.

The stability of [FV-PDI]^− was assessed based on its absorption spectra, which are shown in Figure 3b. The spectrum of the solution exposed to air for 1 h while shielded from light at 298 K (shown in the inset) is almost unchanged. The test was performed over a one-week period, and no significant variations were observed in the spectra, indicating extraordinary stability toward ambient air. This stability is almost unprecedented for PDI radical anions.

The structures of single crystals of FV-PDI and its radical anion [FV-PDI]^− were analyzed to assess the influence of the formation of the radical anion on the structural features. In the crystal of FV-PDI, a unique A and B pair is formed. Figures 5a and 5b show the molecular structure of A, which shows a clear X-shaped geometry with a torsion angle of approximately 35.8°, which is in close agreement with the computed value of 35.37° (Figure S1). The central fulvenic C-C bond linking the two PDI halves is approximately 1.33 Å for A and 1.38 Å for B. These bonds are much shorter than C-C single bonds (1.47 Å), indicating C(sp²)C(sp²) bond character. As a result, the PDI halves are contorted to form shallow bowls with bowl depths of approximately 0.43 Å for A and 0.24 Å for B (Table SS). Figure 5d depicts the packing mode of FV-PDI along the b-axis, in which four crystallographically independent molecules in the A-B-A'-B' sequence are helically arranged, and the neighboring PDI subunits in either A or B are rotated by ca. 73.6° to avoid hindrance between the periphery and the core, and these groups form strong π•••π interactions with a distance of 3.35 Å. Additionally, there are also π•••π (3.20-3.28 Å), C-H•••π (2.8-2.9 Å), and C-H•••O (2.5 Å) interactions between other PDI blades in adjacent molecules.

Crystal structure analysis showed that the radical anion existed as FV-PDI-CoCp₂ when the mixing ratio was 1.2. As shown in Figure 5e-g, the molecular structure is dramatically altered by the presence of CoCp₂, and the π-bowl is deeper (bowl depth of 0.92 Å) than that formed by FV-PDI, probably due to the electrostatic interactions between the PDI radical anion and CoCp₂. Notably, in the reduced state, the two PDI bowls are bent in the same direction due to complexation with CoCp₂.
which is distinctly different from the opposite bowls generated in the neutral state. Compared with the neutral state, the change in the fulvalene bond length in the reduced state is significant, and the length of the central C-C bond has increased to 1.43 Å. Furthermore, the torsion angle between the two PDI subunits was increased to 49.10°. The Co-C bond lengths in the newly synthesized complex are summarized in Table S6. Compared with the values reported for CoCp₂ and [CoCp₂][PF₆]¹⁹ the

Figure 5. Single-crystal structures of FV-PDI and [FV-PDI]⁺: (a) top and (b) side views of molecule A, (c) A and B pairs with strong π•••π interactions, and (d) the packing motif of FV-PDI in the A B A’ B’ sequence with helical arrangements; (e) top and (f) side views, and (g) the packing motif of [FV-PDI]⁺. The green-, purple-, and dark grey-colored atoms are carbon atoms, and the blue-, orange-, and navy-colored atoms represent N, O, and Co, respectively. Hydrogen atoms and long alkyl chains are omitted for clarity.
bond valence sum (BVS) calculation of the Co bonds of FV-PDI-(CoCp)$_2$ gave a value of 3.51; in other words, partial intermolecular charge transfer is occurring between CoCp$_2$ and FV-PDI in the crystal. Additionally, the molecular packing was quite different; one FV-PDI and two CoCp$_2$ molecules are alternately stacked forming a sandwich structure, meaning that the π-π interactions between the PDI cores in the column are absent, and the distance between the Co and perylene centers is approximately 4.62 Å. Furthermore, strong C-H···π interactions with distances of 2.7-2.8 Å and C-H···O interactions with distances of 2.3 Å are formed between the PDI core and the cyclopentadienone moieties of CoCp$_2$, and short π-π···π distances of 3.34-3.39 Å were observed between the PDI blades in adjacent columns. The charge delocalization across the whole conjugated system, the larger torsion angle and the curved planes to relieve strain, and the alternating stacking of positively and negatively charged units all help stabilize the ET complex.

In summary, through precise structural design and reaction optimization, we have achieved the first two-state (neutral and reduced) stable, electron-accepting material and its radical anion. The as-synthesized FV-PDI, based on the carbonyl coupling reaction, showed an experimentally validated LUMO level of -4.38 eV accessible due to full conjugation across the whole molecular skeleton through the fulvalene bridge, which provides sufficient stability and electron affinity. Consequently, the radical anion of [FV-PDI]$^-$ was obtained simply by adding CoCp$_2$ to a solution of FV-PDI. The stability of the radical anion in solution and as solid under ambient conditions is particularly exciting, and complete characterization by UV-vis-NIR, CV, IR and ESR spectroscopic methods as well as single-crystal X-ray diffraction was conducted. Because of the remarkable near-infrared absorption characteristics of this material, further explorations of the magnetic and photothermal therapeutic properties of these radical anions are in progress.

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A two-state (neutral and reduced) stable, electron-accepting material and its radical anion are presented. The formed radical anion ([FV-PDI]⁻) show remarkable stability and near-infrared absorptions extending to 1200 nm. Single-crystal X-ray diffraction analyses revealed that these two states have significantly different molecular shapes and packing arrangements.