

Fluoroperylene diimide: a soluble and air-stable electron acceptor

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A novel soluble and air-stable electron acceptor was reported: due to the fluorination, *N,N'*-diperfluorophenyl-3,4,9,10-perylene-tetracarboxylic diimide (**1**) possessed not only good solubility but also much lower LUMO energy level: -4.37 eV. Furthermore, the photoinduced charge transfer between **1** and PVK was also studied.

Organic electron acceptors, such as C_{60} , carbon nanotube, naphthalene, perylene anhydride and its imide derivatives, have received increasing interest due to their electron transporting ability applicable in *n*-channel organic thin film field-effect transistors (OFETs),^{1–7} organic light-emitting diodes (OLEDs),^{8–10} and organic solar cells.^{11–15} However, most organic electron acceptors are air and moisture sensitive. For example, the OFETs made from fullerenes were easily degraded upon exposure to the air.³ One good approach to solve this problem proved to be by introducing strong electron-withdrawing groups into the π -conjugated system, which can lower the HOMO and LUMO energy levels of a molecule, thus making it less susceptible to oxidation. The OFETs, using copper hexadecafluorophthalocyanine ($F_{16}CuPc$) as the active layer, not only showed high electron mobility of *ca.* 0.03 $cm^2 V^{-1} s^{-1}$ but were also stable in air due to the fact that the fluorination significantly lowered the LUMO energy level of $F_{16}CuPc$.² Fluorinated naphthalene diimides also exhibited similar characteristics of high electron mobility (*ca.* 0.06 $cm^2 V^{-1} s^{-1}$) and excellent stability in air, and solubility in aromatic solvents.⁵

We have designed and synthesized a novel fluorinated perylene diimide, *N,N'*-diperfluorophenyl-3,4,9,10-perylene-tetracarboxylic diimide (**1**), whose much lower LUMO energy level, stronger electron accepting ability and good solubility were characterized. For comparison, the non-fluorinated analog of **1**, *N,N'*-diphenyl-3,4,9,10-perylene-tetracarboxylic diimide (**2**), was also prepared according to the same procedure.[†]

Fig. 1 depicts the UV-Vis spectra of the solutions of **1** and **2** in DMF. It was found that **2** had three absorption bands at 457, 488, and 524 nm assigned to the π - π^* transitions in the

perylene ring, while the three absorption peaks of **1** were red-shifted about 5 nm compared to those of **2**. This observation suggested that the solvation of **1** was stronger than that of **2** due to the introduction of the high electronegative F atoms in **1**. It could be proved by the fact that **1** was soluble in many common solvents, such as THF, acetone, chloroform, toluene, xylene, dioxane, *etc.*, with the maximum solubility of several thousand (wt%), while compound **2** was only slightly soluble in strong polar solvents, such as DMF and DMSO. Based on these data, we believe that the fluorination changed the polarity of perylene diimide, resulting in impressive improvement of the solubility of **1**.

It was interesting to notice that compound **1** showed absorption peaks between 600 and 900 nm (see the inset in Fig. 1), which originated from the radical anion of **1** ($1^{\cdot-}$).¹⁶ It could be explained that compound **1** was a strong electron acceptor due to the attachment of the two electron-deficient perfluorinated phenyl groups to perylene moiety, and the excited **1** could obtain an electron easily from the weak electron donor such as DMF to form radical anion $1^{\cdot-}$ in the presence of water and air. The formed $1^{\cdot-}$ was stable due to the high π -conjugation of the perylene ring and the strong attraction of the two perfluorinated phenyl groups. This was distinctly different from non-fluorinated perylene diimides, for instance, *N,N'*-di(3,6-xylyl)-3,4,9,10-perylene-tetracarboxylic diimide (**3**) reduced to form a radical anion only at certain negative potentials through the electrochemical method.¹⁶

The stability of the radical anion $1^{\cdot-}$ could be supported by the cyclic voltammograms from compounds **1** and **2** (Fig. 2). The cyclic voltammogram of **1** in DMF solution showed two reversible reduction peaks, indicating that **1** could accept two electrons. The half-wave reduction potential ($E_{-1/2}$) for $1^{\cdot-}$ formation was -0.37 eV (*vs* SCE), 0.14 eV more positive than that for $2^{\cdot-}$ formation, suggesting a stronger electron-withdrawing ability of compound **1**. Since we did the CV measurements in ambient air, the measured solution must contain a very small amount of water and O_2 molecules, the reduction potential of O_2 should appear more negatively than that of standard O_2 electrode. We noted that both reversible

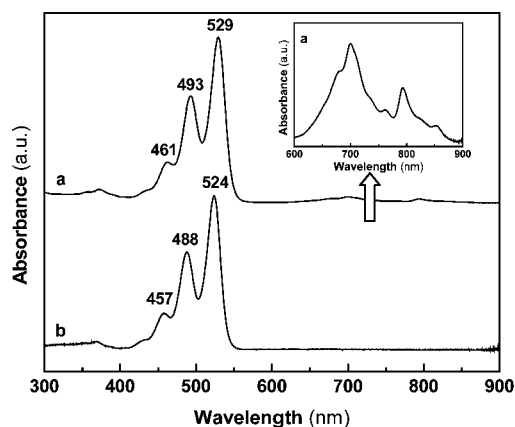


Fig. 1 UV-Vis spectra of compounds **1** (a) and **2** (b) in DMF solutions. Inset is the enlarged spectrum for **1** between 600 and 900 nm.

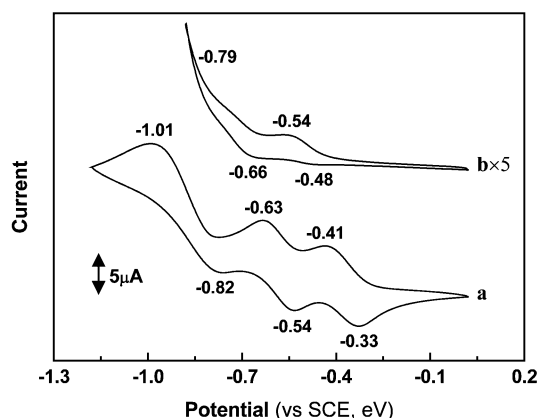


Fig. 2 Cyclic voltammograms of compounds (a) **1** and (b) **2** (magnified by 5) in DMF solutions; scanning rate 50 $mV s^{-1}$.

reduction peaks of compound **1** were more positive than that of O₂. It means that the electronegativity of **1** is even stronger than that of O₂ in our case, and this makes it less susceptible to oxidation. Following this argument, it is expected that the devices prepared from **1** would be stable in a surrounding where the concentrations of O₂ and H₂O were not too high.

In order to study the influence of fluorination on the electron accepting ability of the excited perylene diimide molecules, we investigated the photoconductivities of compounds **1** and **2** doped in poly(*N*-vinyl carbazole) (PVK), a good hole-transportation material, in single-layered photoreceptors (SLPRs). The photoconductivities were measured by the standard xerographic photoinduced discharge technology, where the surfaces of SLPR were corona charged negatively or positively.¹⁷ Their photoconductive properties were evaluated by the photoinduced discharge curves (PIDCs) under illumination at different monochromatic wavelengths. From PIDC, we obtained $E_{1/2}$, the exposure energy required for SLPRs to reduce the surface potential to half its original value. The reciprocal of $E_{1/2}$ can indicate photosensitivity ($1/E_{1/2}$). The bigger the $1/E_{1/2}$ is, the higher the photosensitivity is.¹⁷

Fig. 3 depicted the photosensitivities of compounds **1** and **2** doped in PVK (1 : 80 by wt) when exposed to various monochromatic wavelengths. It was observed clearly that the **1**-PVK composite exhibited much better photoconductivity than the **2**-PVK composite did whether charged negatively or positively. The results were reasonable. Since the LUMO and HOMO energy levels of **1** are lower than those of **2** due to the fluorination, it is much easier for the excited compound **1** to get an electron from the electron-donor PVK than **2**, resulting in a higher exciton dissociation efficiency for the **1**-PVK composite, and subsequently, its photosensitivity increased by over 20 times compared with that of the **2**-PVK composite. It was also noticed that, under positive charging, the **1**-PVK composite showed extremely excellent photosensitivities relative to those of the **2**-PVK composite. It was thought that the electron transport channels formed from the molecules of **1**, similar to the electron transport channels formed from C₆₀ molecules in the PPV-C₆₀ composite,¹⁵ might exist in the **1**-PVK composite due to the good solubility of **1** and the electron transporting ability of perylene diimide, thus, the photogenerated free

electrons could move easily to the surface of the SLPR through these channels to neutralize the positive charges there, leading to improved photosensitivities of the **1**-PVK composite.

In conclusion, a soluble and air-stable electron acceptor, *N,N'*-diperfluorophenyl-3,4,9,10-perylenetetracarboxylic diimide (**1**), was designed and prepared. By introducing strong electron-withdrawing F atoms, compound **1** was sufficiently electron deficient to yield a stable radical anion in air. Improved photoconductivity was observed in compound **1** due to its lower LUMO energy level caused by fluorination. It is believed that such fluorinated compounds with good solubility and stability in air will have potential application in organic electronic and optoelectronic devices.

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Notes and references

† Compounds **1** and **2** were prepared according to the procedure described in ref. 5. *Analytical and spectroscopic data*: for **1**, anal. calcd for C₃₆H₈F₁₀N₂O₄: C, 59.85; H, 1.12; N, 3.88. Found: C, 59.74; H, 0.99; N, 3.82%; ¹H NMR (500 MHz, CDCl₃, TMS): δ = 8.82 (d, *J* = 8 Hz, 4H), 8.76 (d, *J* = 8 Hz, 4H); FTIR (KBr, pellet): ν/cm⁻¹ 1721, 1685 (C=O); UV-Vis (toluene): λ_{max}/nm (ε) = 529 (74000), 493 (46700), 461 (17500). For **2**, FTIR (KBr, pellet): ν/cm⁻¹ = 1703, 1665 (C=O); anal. calcd for C₃₆H₁₈N₂O₄: C, 79.70; H, 3.34; N, 5.16. Found: C, 78.88; H, 2.95; N, 5.12%.

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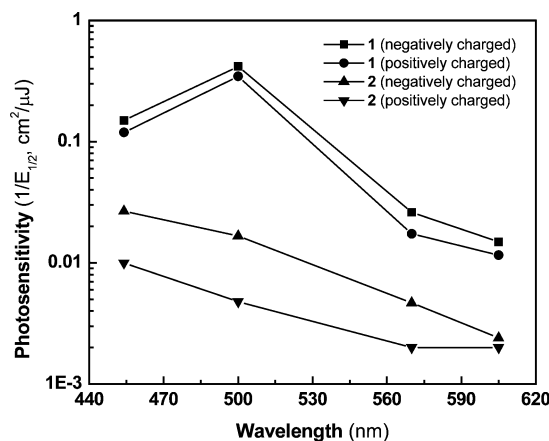


Fig. 3 Photosensitivities of **1**-PVK and **2**-PVK composites (1 : 80 by wt) when exposed to various monochromatic wavelengths; exposure intensity 30 μW cm⁻².