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Sulfur-substituted perylene diimides: efficient tuning of LUMO levels and visible-light absorption *via* sulfur redox†

Yongxin Zhou,[a] Bo Xue,[a] Chenyu Wu,[b] Siqi Chen,[a] Hui Liu,[a] Tonggang Jiu,[c] Zhibo Li[a] and Yingjie Zhao*[a]

A series of sulfide and sulfone substituted perylene diimides (PDIs) with different LUMO levels covering a range of 0.72 eV were synthesized through simple sulfur redox chemistry. The LUMO level of phenylsulfone substituted PDI reached a record-breaking −4.75 eV. In addition, the maximum emission ranged from 540 to 692 nm.

Perylene diimides (PDIs) have been recognized as promising electron acceptor materials for n-type semiconductors owing to their low-lying lowest unoccupied molecular orbital (LUMO) levels and highly reversible redox waves in cyclic voltammetry (CV).[1–9] Recently, the electron deficient π surfaces of PDIs have been drawing attention because they can attract anions or anionic intermediates which make them suitable candidates for sensing, anion binding, transport, and anion–π catalysis.[10–13] In addition, PDIs exhibit other interesting properties—such as high fluorescence quantum yields, high photochemical stability and low cost, which allow PDIs to be used in many other newly developed applications.[14–20] Among all these PDIs and applications, the low-lying LUMO level was considered as a key point to result in excellent n-channel performances and make them attractive to assemble into complex architectures. The low-lying LUMO level could reduce the energy barrier between the Fermi level of the source and drain contacts of the semiconductor and therefore facilitate electron injection and transportation.[3,21–24] In addition, the optimized LUMO level could enhance the ambient stability of PDIs in the presence of impurities such as water and oxygen. On the other hand, related to these low LUMOs, the intrinsic positive quadrupole moment of these PDIs which results in electron-deficient aromatic planes can be influenced. As a result, when the reactions undergo an anionic transition state, the anionic intermediates can be stabilized by the anion–π interactions between the electron-deficient surface and the intermediates to finally achieve the catalysis purpose[13,25] Some applications have been realized including anion binding, transport across lipid bilayer membranes, and catalysis of reactions with anionic transition states.[10–13] Although PDIs have promising characteristics, a detailed investigation into the control of the energy levels has been less reported.[10,26] Therefore, we are particularly interested in making π-expanded PDIs featuring low-lying LUMO levels. PDI molecules can be easily functionalized at the core by introducing functional groups to the "bay" positions to tune the reduction potential and the LUMO levels. Some efforts have been devoted to functionalize the π-surface of the PDIs to lower the LUMO energy level.[10,27,28] –CN, $-NO_2$, and –F, which are all classical electron-drawing groups, have been introduced into the π-surface to improve the electron-transport and ambient stability.[27–31] Herein, we studied sulfur-substituted perylene diimides at the bay positions of PDIs. Sulfur bridges were particularly attractive for varying the LUMO energy level through simple and robust sulfide oxidation chemistry.[13,32,33] The electron-donating sulfide can be converted *in situ* into strong electron-withdrawing sulfone acceptors and avoid reductive radical formation. The LUMO levels of naphthalenediimides (NDIs) have been well studied by Matile and co-workers through the sulfide oxidation chemistry.[10,13,32–35] Regular different π-acidity surface and LUMO levels of NDIs could be obtained for attracting the anionic intermediate. In this work, LUMO levels of the PDIs ranging from −4.03 to −4.75 eV were achieved. LUMO levels as low as −4.75 eV were realized (compound **8**) among the obtained PDIs. These innovative PDIs with low LUMO levels are of interest as electron transporters in n-type semiconductor materials and also have some significance for the study of anion–π interactions and anion–π catalysis.

The structures and synthesis of the sulfide and sulfone PDIs (**2–9**) are shown in Fig. S1 (ESI†). The details of all the synthesis procedures are listed in the ESI.† For the ultimate goal

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[a] *Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education Department, College of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: yz@qust.edu.cn*
[b] *University of New South Wales, Sydney, New South Wales 2018, Australia*
[c] *Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, P. R. China*

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compound **9** from **6**, even under extremely harsh conditions, no target product was obtained. We did observe the existence of **9** in the reaction mixture by MALDI-TOF mass spectrometry. However, the separation of **9** has so far not been successful. The aromatic core of **9** is probably too electron deficient to exist. All of the products show good solubility in common organic solvents at room temperature.

The different substituted PDIs were characterized by absorption and fluorescence spectroscopy first (Fig. 1 and 2). The unsubstituted PDI (**1**) was used as a reference compound here. The incorporation of the substituents with different electron donating and accepting effects on the bay region significantly affects the absorption and fluorescence properties in solution. Compared to **1** (λ_{abs} = 523 nm, λ_{em} = 540 nm), the absorption and fluorescence maximum of **2** with electron-donating alkylsulfide substituent groups shifted to 560 nm and 692 nm. The Stokes shift changed from 17 nm to 132 nm. However, the fluorescence quantum yield decreased from 95% to 3.6%. The oxidation of the arylsulfoxide to arylsulfone reverted the electron-donating nature into strong electron-withdrawing acceptors. The absorption and fluorescence maximum of **7** blue shifted back to λ_{abs} = 527 nm and λ_{em} = 565 nm. The fluorescence quantum yield increased to 98%. For the phenyl series, similar tendency was observed. The absorption and fluorescence maximum of **3** are λ_{abs} = 552 nm and λ_{em} = 678 nm which are slightly blue shifted compared to **2** which may be due to the conjugation effect of the aromatic benzene group. Oxidation of **3** gave **8** with λ_{abs} = 542 nm and λ_{em} = 582 nm. The fluorescence quantum yield changed from 0.9% for **3** to 95% for **8**. Interestingly, for pentafluorophenylsulfide substituted **6**, no obvious red shift was observed compared to **1**. The absorption maximum is λ_{abs} = 531 nm which is only 8 nm red shift. However, the fluorescence maximum of **6** red shifted to λ_{em} = 637 nm (97 nm red shift compared to **1**). In addition, the fluorescence quantum yield remains at 34%. This result is interesting because this may provide a way to construct near-infrared fluorescent dye with high fluorescence quantum yield by the dual effect of the pentafluorophenyl and the sulfide.

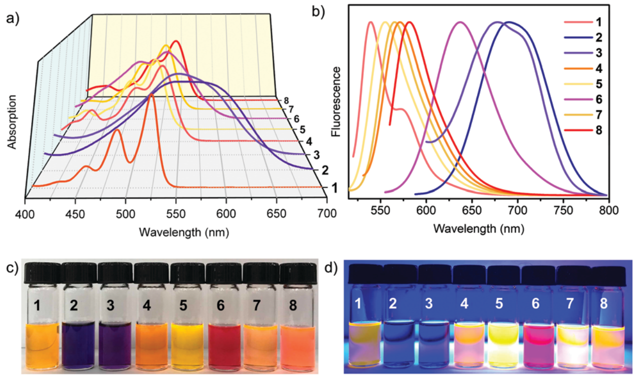
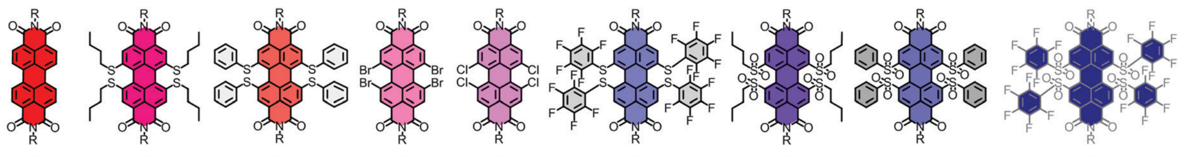


Fig. 2 Absorption (a) and fluorescence (b) spectra of the different substituted PDIs in CH_2Cl_2, normalized to maxima; pictures of PDIs under sunlight (c) and 365 nm UV light (d).

The LUMO energy levels of compounds **1–8** were determined by CV in CH_2Cl_2 against the ferrocenium/ferrocene (Fc^+/Fc) couple as the internal standard (Fig. S19, ESI†). All the compounds exhibit two distinct, reversible reduction steps.

The energy level of the LUMO was calculated by assuming −5.1 eV for Fc^+/Fc. The LUMO levels are summarized in Fig. 1. The LUMO level of the alkylsulfide substituted **2** is −4.06 eV which is similar to that of the unsubstituted **1** (−4.03 eV). This indicated that the alkylsulfide substituent group had very little influence on the π-surface of PDI. However, the phenylsulfide substituent group shows obvious electron-withdrawing character which lowers down the LUMO level to −4.15 eV (**3**). The LUMO level of **6** with two electron-withdrawing pentafluorophenylsulfide groups was found to be −4.37 eV. Full oxidation of the four sulfide groups in **2**, **3** led to sulfone groups and lowered the LUMO levels by 0.65 eV and 0.60 eV to −4.71 eV for **7** and −4.75 eV for **8** respectively. Partial oxidation of the sulfide will lead to sulfoxide groups which is also an electron withdrawing group. The electron withdrawing ability of the sulfoxide is between the sulfide and sulfone. We did observe the sulfoxide intermediates by MALDI-TOF mass spectrometry and Thin-Layer



	1	2	3	4	5	6	7	8	9
LUMO [eV][a]	-4.03	-4.06	-4.15	-4.24	-4.28	-4.37	-4.71	-4.75	-4.80[b]
abs_{max} [nm]	523	560	552	529	517	531	527	542	/
em_{max} [nm][c]	540	692	678	571	555	637	565	582	/
φ_f[d]	95%	3.6%	0.9%	63%	93%	34%	98%	95%	/

Fig. 1 Summary of electrochemical and photophysical properties of compounds **1–9**. [a] LUMO energies were obtained by CV and are reported in electron volts relative to −5.1 eV for Fc^+/Fc; [b] the LUMO energy level of **9** was calculated at the B3LYP/6-31+G** level of theory; [c] the emission spectra were excited at abs_{max}; [d] the fluorescence quantum yield of the PDIs was determined by using **1** as the standard. All the measurements were done in CH_2Cl_2 at room temperature (1×10^{-5} M).

Chromatography. However, no separation and purification were done because the chirality of the sulfoxide bridges makes the substituted PDIs complicated on the one hand and the purpose of this work is pursuing extremely low LUMO level of the PDIs on the other hand. The LUMO value of −4.75 eV obtained for **8** is already remarkable. To the best of our knowledge, this is the lowest LUMO level for the reported PDI derivatives. The unsuccessful synthesis and separation of **9** is possibly attributed to the too low LUMO which makes it unstable in the air. The calculated LUMO of **9** by DFT at the B3LYP/6-31G** level is −4.80 eV which is reasonable and consistent with the changing tendency. The pentafluorophenyl together with the sulfone led to an extremely low LUMO level of **9**. Besides, we also measured the LUMO level of the well-known compounds **4** and **5** which shows a value of −4.24 eV and −4.28 eV as control experiments. These values are in accordance with the previously reported results.

To elucidate the structure–property relationships behind these observed property changes by structure variation of the PDI derivatives, we subsequently performed density functional theory (DFT) calculations at the B3LYP/6-31+G** level of theory using the Gaussian 09 D01 software package to obtain geometry-optimized structures and frontier molecular orbital information of dyes **1–9** (Fig. 3). All the alkyl chains were simplified to the methyl substituent to reduce the computation time as a common practice. Time-dependent (TD) DFT calculations were performed to reveal the contribution of the transition between the highest occupied molecular orbital (HOMO) and the LUMO to the lowest singlet excited state (S_1) excitation (Fig. 3, below the dye labels). Although DFT calculations for these PDI derivatives tend to overestimate the exact LUMO energy levels by 0.1–0.5 eV compared with the experimentally measured values (Fig. 1), the general tendency is mainly the same, where more electron-withdrawing substituents tend to lower the LUMO energy level. More electron-withdrawing substituents are known to yield lower LUMO energy levels given the same chromophore.[36,37] This trend generally complies with our experimental observation for **1–9** that more electron-withdrawing substituents indeed lead to lower LUMO energy levels, despite some slight deviation within experimental errors. In particular, **9** was calculated to exhibit a LUMO energy level of −4.80 eV, lower than any of the dyes **1–8**, despite the overestimation by DFT computation. Indeed, the highly electro-withdrawing pentafluorophenyl groups and sulfoxide groups add up to the most electro-withdrawing substituents among the substituents of all the dyes. As TD-DFT calculations reveal that all of the dyes **1–9** have a S_1 excitation with 98% contribution from HOMO → LUMO transitions, it is rational to use HOMO and LUMO energy levels to discuss their λ_{abs}. Indeed, a narrower HOMO–LUMO energy gap should lead to more red-shifted absorption/fluorescence by requiring less excitation energy.[38] Particular attention was drawn to **2** and **3** which exhibit significantly red-shifted visible-light absorption compared to other dyes, while the absorption peak of **6** also displays some red shift (Fig. 2a). By examining the visualized frontier orbitals of **2**, **3** and **6**, we clearly observed a significant portion of HOMO localized on the S atoms, each of which has two pairs of lone electrons. Because there is no LUMO on the S atom for each of the three dyes, apparently the substituents attached to S have a significant effect on the HOMOs, but should have much less impact on the LUMOs. Indeed, the highly electro-donating

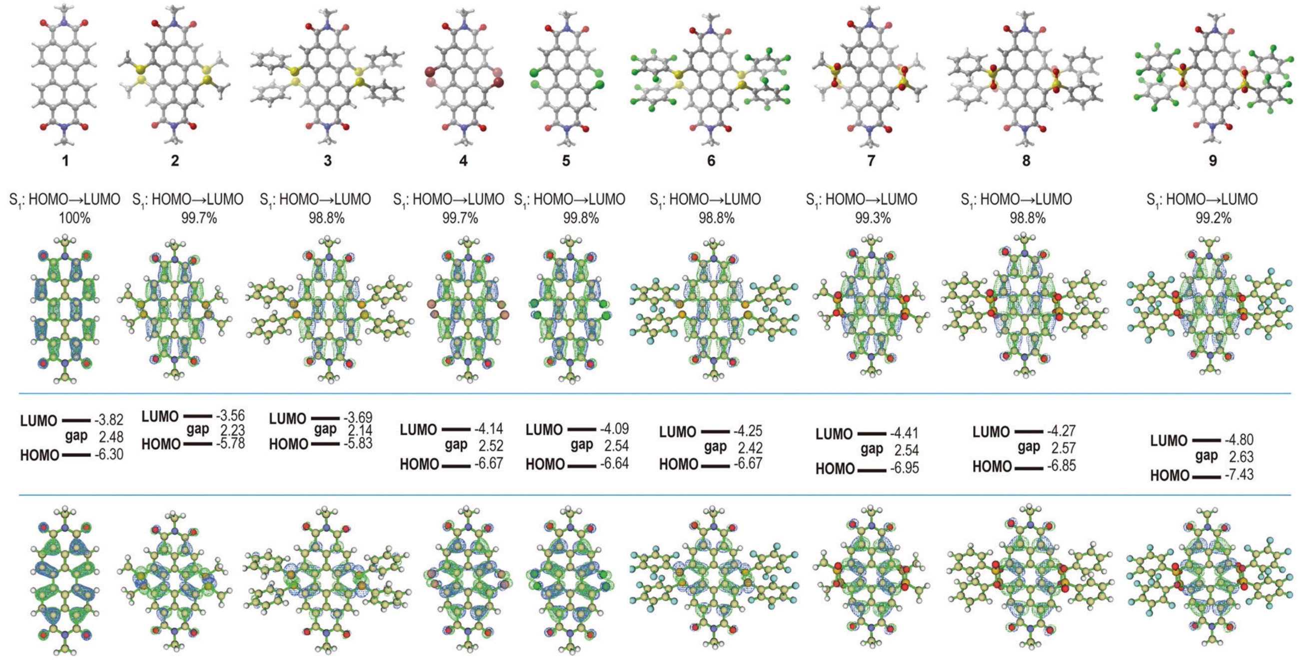


Fig. 3 Molecular geometries (top) and visualized frontier orbitals (isovalue = 0.03, bottom) of PDI derivatives **1–9**, calculated at the B3LYP/6-31+G** level of theory. HOMO and LUMO energy levels and their gaps were denoted in eV. Contribution of HOMO → LUMO transition to S_1 excitation was denoted below the dye label.

alkylsulfide groups of **2** and similarly highly electro-donating phenylsulfide groups of **3** significantly move their respective HOMO energy levels up but not notably affect their LUMO energy levels, which end up with a much narrowed HOMO/LUMO energy gap, leading to much red-shifted visible-light absorption. The pentafluorophenylsulfide groups of **6** have five F atoms in each, which greatly reduces the electron-donating ability, thus only leading to a limited narrowing effect on the HOMO/LUMO energy gap and relatively a slight red-shift in absorption. Additionally, it occurs that the sulphide substitution could also quench fluorescence and yield much lowered φ_f, resulting from partial n → π* charge transfer character (from sulfide to the PDI core) of the S_1 excitation. Indeed, charge transfer has been widely reported to retard the fluorescence rate constant and thus largely quench the fluorescence.[39,40]

In summary, by using simple sulfur redox chemistry, we successfully realized the introduction of sulfide and sulfone substituted groups into the PDI π-surface which provided access to tune the LUMO levels, covering a range of 0.72 eV. A LUMO level lower than −4.75 eV was obtained from the phenylsulfone substituted PDI (**8**) which is the lowest LUMO of the reported PDI derivatives so far. These PDIs with different LUMO levels could be used as n-type semiconductor materials on the one hand. On the other hand, due to electron deficient π surfaces, the obtained PDIs are ideal to integrate anion–π interactions into functional systems. In addition, the pentafluorophenylsulfide substituted group was introduced into the PDI core for the first time. The dual effects of the electron donating S and the withdrawing F together with the electron deficient PDI surface construct a unique D–A–D system. In the end, the influence and the change in trend of the photophysical properties of the obtained PDI series by the different substituted groups were also studied. With electron-donating and withdrawing substituents in the core, the PDI chemistry becomes colorful. The maximum emission ranged from 540 to 692 nm. A maximal 132 nm Stokes shift was observed for the alkylsulfide substituted PDI (**2**). The pentafluorophenylsulfide substituted PDI (**6**) maintained both the fluorescence quantum yields and the long wavelength fluorescence.

Conflicts of interest

There are no conflicts to declare.

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