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# Synthesis, characterization, photophysical properties and stability of bay-substituted tetrachloro-perylene diimide dianion salt by alkali treatment

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### ABSTRACT

Bay-substituted tetrachloro-perylene diimide dianion salt was synthesized facilely by using  $K_2CO_3$  as reducing agent. The structure was confirmed by using a very thorough analysis based on the data from <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV–vis spectra. Perylene diimide dianion salt shows high stable characteristic in the air or in some specific solutions such as acidic solution or oxidizing metal ion dissolved in deionized water under solid condition. However, the dianion converts slowly into corresponding radical and neutral perylene diimide in alkali solutions. Furthermore, the perylene diimide dianion salt has high HOMO and LUMO energy levels in comparison with that of corresponding neutral perylene diimide derivatives.

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### 1. Introduction

Perylene diimide (PDI) and its derivatives which are important n-type organic semiconductors have attracted more and more attention due to the potential application in solar cell, organic field effect transistors, light-emitting devices and bio-sensing etc.<sup>1–5</sup> Due to its unique molecular structure and deficient-electron properties, pervlene diimide possess the lower potential to obtain easily one electronic or two electronics to convert into the corresponding radical anion or dianion.<sup>6–10</sup> There do exist some of the similar properties between the radical anions of perylene diimide derivatives and other aromatic radical species, such as high reducibility and alkalinity.<sup>11,12</sup> Further more, perylene diimide also showed high photo-thermal conversion.<sup>13,14</sup> Although a number of methods have been reported for the preparation of perylene diimide radical anion or dianion, including electrochemical reduction, chemical reduction, intermolecular electron transfer and intramolecular electron transfer.<sup>15–19</sup> Little pieces of work in the literature have reported about the isolated and solid stable perylene diimide radical anions in addition to our group. In a recent study, one facile method was employed for the preparation of the PDIs

radical anion, here known as alkali treatment method.<sup>12</sup> We regrettably did not get the perylene diimide dianion using this method. An example of the first successful preparation of the isolated, ambient stable perylene diimide dianion was reported by F. Würthner and coworkers,<sup>20</sup> which described the detailed method steps for preparing PDIs dianion and its preparation conditions, in particular the requirement for the special structure (a highly electron deficient PDIs) and the harsh reaction condition (such as Pd/C–H<sub>2</sub> as catalyzer and under nitrogen atmosphere). This is an inspiration for us to understand that the low reduction potential is essential for the successful preparation of PDIs dianion, which also means that the high reduction potential is the main factor hindering the successful preparation of dianion in our previous study.

Due to introduction of strong electron-withdrawing groups such as chlorine atom, the trifluoromethyl etc. the perylene diimide derivatives possess a system of electron deficient and low reduction potential properties.<sup>21–23</sup> Thus, in this paper, we take tetrachloroperylene diimide derivatives (TCIPDI) with first reduction potential (-0.098 ev) as the object of this study, combined with our previous work to prepare the PDIs dianion salt. Subsequently, the performance of the prepared PDIs dianion salt was successfully tested in various environments such as acidity, alkalinity, solvation, and oxidizing metal ions.

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### 2. Results and discussion

### 2.1. Synthesis and structure characterization

Scheme 1 depicts the chemical structures and synthetic routes of TCIPDI dianion salt. Synthesis starts from an imidization of 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride by reaction with cyclohexylamine, giving TCIPDI with a yield of ca. 85%.<sup>24</sup> The reaction was carried out by heating TCIPDI and K<sub>2</sub>CO<sub>3</sub> at 85 °C for 8 h with reflux to stop the reaction, subsequently, after a purification operation, a high purity CTCIPDI dianion salt could be obtained,<sup>24</sup> giving TCIPDI dianion salt with a high yield of ca. 80%. Chemical structure of TCIPDI dianion salt was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV–vis spectrum, and detailed synthetic procedures and product characterization are provided in the experimental section.

Referring to the literature reported by F. Würthner and coworkers (Chem. Sci., 2015, 6, 1663.), Elijah Shirman and coworkers (Journal of Physical Chemistry B, 2008, 112 (30):8855-8858.), we proposed its concrete structure showed in Fig. 1 a. Comparing the IR spectra of TCIPDI with that of TCIPDI dianion salt (Fig. 1b), there emerged a new absorption peak at 1129 cm<sup>-1</sup>, which could be ascribed to the C–O stretch vibration of the aromatic ether caused by C=O reduction. Meanwhile, significant differences were observed in other region, specifically spectra somehow shifted from 1703 cm<sup>-1</sup> for amido groups, 1666 cm<sup>-1</sup> for carbonyl groups, 1587 cm<sup>-1</sup> for C–H of aromatic ring to 1697 cm<sup>-1</sup>, 1649 cm<sup>-1</sup> and 1639 cm<sup>-1</sup>, 1557 cm<sup>-1</sup>, respectively. More importantly, the stretching vibration of carbonyl for TCIPDI dianion split into two peaks (1649  $\text{cm}^{-1}$  and 1639  $\text{cm}^{-1}$ ), conforming that some of the additional electron density of double-reduced TCIPDI is localized in the C=O and core C=C  $\pi^*$  orbitals. More robust evidence came from the <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra of TCIPDI and its dianion salt. The chemical shift of proton in perylene diimide core for the neutral TCIPDI appeared at 8.658 ppm (Fig. 1c). Which was consistent with similar PDIs.<sup>25</sup> However, the chemical shift of proton in pervlene diimide core for TCIPDI dianion salt was obviously shifted toward the higher field, with splitting into four single peaks, located at 8.496 ppm, 8.345 ppm, 7.436 ppm and 6.845 ppm, respectively (perylene diimide core for the neutral TCIPDI: 8.658 ppm). Referring to the literature mentioned above: F. Würthner and coworkers, Shirman and coworkers, together with taking the distribution of electron cloud over  $C-O^-$  is more concentrated than that over C=O and the Coulombic repulsion between the dianion into considering, we give the following explanation: As for the hydrogen atom at position 1, the electron cloud density of this H is largest due to the dual effect of the delocalized electron clouds attributed to its parent molecule and the adjacent molecules distributed on the  $C-O^{-}$ , thus leading to the strongest magnetic field shielding, so the corresponding nuclear magnetic signal peak shifted the largest to the high field. For the hydrogen atom at position 2, it is influenced by the electron clouds delocalized on the  $C-O^-$  of its parent molecule and that on the C=Oof the adjacent molecules, causing the second largest chemical shift. For the hydrogen atom at position 3, it is influenced by the electron clouds delocalized on the C=O of its parent molecule and

that on the  $C-O^{-}$  of the adjacent molecules. Due to the Coulombic repulsion between the dianion, the electron cloud density is less concentrated compared to the hydrogen atom at position 2, causing the third largest chemical shift. For the hydrogen atom at position 4, it is influenced by the electron clouds delocalized on the C=O of its parent molecule and that on the C=O of the adjacent molecules. resulting in the least chemical shift. Further evidence came from the corresponding <sup>13</sup>C NMR (Fig. 1d), as for the TClPDI, the chemical shift of carbons located in different chemical environments caused by the strong electron-withdrawing groups such as four chlorine atoms at bay position and the amide groups appeared at 162.66 ppm, 135.28 ppm, 132.89 ppm, 131.39 ppm, 128.38 ppm, 123.74 ppm, 123.32 ppm, which represented the carbon atoms located at the position from 1 to 7, respectively. This was also consistent with the literature.<sup>26</sup> For TCIPDI dianion salt, the signals of different chemical shift of carbons were interesting, with 18 signal peaks emerging at 170.09 ppm, 163.60 ppm, 163.36 ppm, 147.22 ppm, 139.20 ppm, 135.10 ppm, 134 ppm, 132.80 ppm, 131.35 ppm, 129.90 ppm, 129.83 ppm, 126.90 ppm, 125.89 ppm, 123.14 ppm, 119.20 ppm, 115.51 ppm, 112.03 ppm, 109.94 ppm, which represented the carbon atoms of TCIPDI dianion salt located at the position from 18 to 1. The potential reason may be still related to the density of the outer electron cloud, the more concentrated the density of the electron cloud, the stronger the shielding effect on the external magnetic field, resulting in the  $\delta$  value moving to the high field direction.

### 2.2. Optical and electrochemical properties

For characterizing the basic structure and properties of pervlene diimide dianion, UV-vis absorption spectrum and the fluorescence emission spectrum are essential for the study.<sup>27</sup> In general, the pervlene diimide dianion showed a red-shifted UV-vis absorption and a weak fluorescence emission compared with those of neutral perylene diimide<sup>27</sup>(Fig. 2). TCIPDI exhibited the maximum characteristic absorption bands at 518 nm and 482 nm, belonging to 0-0 and 0-1 electron transition, respectively. Furthermore, TClPDI showed strong fluorescence with maximum peak at 554 nm under concentration of  $10^{-6}$  M. On the contrary, compared with the strong fluorescence emission of the TCIPDI, TCIPDI dianion salt exhibited much weaker fluorescence with maximum peak at 763 nm even under concentration of  $10^{-5}$  M. The characteristic absorption peak at 610 nm for TCIPDI dianion was observed in UV-vis spectra, which indicated the formation of pervlene diimide dianion.<sup>27</sup> In addition, the presence of the weak fluorescence was also one favourable evidence for the formation of pervlene diimide dianion. The cyclic voltammograms of TCIPDI and its dianion salt were illustrated in Fig. 3. In combination of the CV results, TCIPDI underwent two quasi-reversible one-electron reduction waves with potentials of  $E_{1/2}$  (TClPDI/TClPDI<sup>-</sup>) = -0.019 V and  $E_{1/2}$  $(TCIPDI^{-}/TCIPDI^{2-}) = -0.240$  V (vs. Ag/AgCl) in N,N-Dimethylformamide. However, the cyclic voltammetry of TCIPDI dianion salt exhibited disappearance of the reduction waves corresponding to the two reduction waves of TCIPDI whether it was from zero to negative to zero or when applied positive potential. Thus we assumed that owing to the delocalized electron cloud, the



Scheme 1. Synthetic routes of TCIPDI dianion salt.

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Fig. 1. (a) Chemical structure of the TCIPDI dianion salt (b) FT-IR spectra of TCIPDI and TCIPDI dianion salt (c) <sup>1</sup>H NMR spectra of TCIPDI and TCIPDI dianion salt (d) <sup>13</sup>C NMR spectra of TCIPDI and TCIPDI dianion salt.



**Fig. 2.** Absorption and fluorescence spectra of TCIPDI (Concentration:  $1 \times 10^{-6}$  M) and TCIPDI dianion salt (Concentration:  $1 \times 10^{-5}$  M) (excitation wavelength: 500 nm for TCIPDI and 600 nm for TCIPDI dianion salt).

interaction between the potassium and the oxygen atoms belonging to the carbonyl groups, the adjacent hydrogen atoms, and a large number of solvent molecules, all of these contributed to making the overall stability of the whole, leading to the difficulty of being oxidized.



Fig. 3. Cyclic voltammograms of TCIPDI and its dianion salt recorded in DMF containing 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> at 0.1 Vs<sup>-1</sup>.

# 2.3. Influence of the acidic and alkaili on the optical properties of TCIPDI dianion salt

Based on the previous study, the radical anion of PDIs had a clear response to the acid, which is accompanied by the characteristic absorption of the radical anion of PDIs in the UV absorption spectrum with the amount of acid increased gradually decreased until the final return to the neutral PDIs.<sup>12</sup> Surprisingly, when titrated

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**Fig. 4.** (a) UV–vis spectra of TCIPDI dianion salt titrated with concentrated nitric acid. (the mass fraction: 68%) (b) UV–vis spectra of TCIPDI dianion salt titrated with NaOH aqueous solution (concentration:  $10^{-2}$  M) (c) UV–vis spectra of TCIPDI dianion salt titrated with large excess of Fe<sup>3+</sup> aqueous solution (d) UV–vis spectra of TCIPDI dianion salt in different solvents (Concentration of TCIPDI dianion salt:  $5 \times 10^{-5}$  M).

with hydrochloric acid, acetic acid, terephthalic acid (Supporting information S1–S3) or concentrated nitric acid (Fig. 4a), the UV absorption spectrum did not show what we had expected, but remained essentially unchanged, suggesting the dianion did not show alkaline. However, when titrated with NaOH aqueous solution under concentration of  $10^{-2}$  M, the UV absorption spectrum had undergone tremendous changes (Fig. 4b), the specific performance: a new characteristic absorption peak emerged at 516 nm, and at the same time, there appeared a strong absorption peak at 784 nm, we attributed the former to the 0-0 electron transition of neutral TCIPDI, and the latter should belong to the characteristic peaks of radical anion.

Furthermore, according to our previous report, the radical anion of PDIs showed the strong reducibility, which can reduce most of the metal ions (such as:  $Fe^{3+}$ ,  $Cu^{2+}$  etc.) corresponding elemental or low valence cations.<sup>12</sup> Whereas UV–vis spectrum of the TCIPDI dianion salt hardly showed any changes but only the decreasing of intensity when adding  $Fe^{3+}$  or  $Cu^{2+}$  at low concentration (Surpptiong information S4, S5), indicating TCIPDI dianion did not have sufficient reduction power to reduce  $Fe^{3+}$  or  $Cu^{2+}$ . But when titrated TCIPDI dianion salt solution with large excess of FeCl<sub>3</sub> (Fig. 4c) or CuCl<sub>2</sub> (Surpptiong information S6), The absorption changes were observed located in the UV-region. Referring to the work of Mogens Brøndsted Nielsen et al. (*Chemical Communications.* 2008, 112 (17): 1986–1988.), the absorption spectra corresponded to a superposition of that of the metal complex of FeCl<sub>3</sub> or CuCl<sub>2</sub> alone and that of TCIPDI dianion salt, meanwhile, the complexation did not alter the characteristic absorption peak of TCIPDI dianion salt located at 610 nm, which indicated TCIPDI dianion salt was no longer reacted with metal ions by the oxidation-reduction reaction mechanism, and more was present as complexes in the presence of high concentrations of metal ions. Typically, in previous reports, PDIs radical anion did not show the characteristic peaks of the radical anion when using CH<sub>2</sub>Cl<sub>2</sub> as solvent.<sup>28</sup> However, further investigation showed that the TCIPDI dianion salt dissolved in different solvents (such as: CH<sub>2</sub>Cl<sub>2</sub>, DMF, THF, Acetone and etc.) had exhibited the same optical characteristic band of the dianion (Fig. 4d), indicating there existed a fundamental difference when comparing TCIPDI dianion with other PDIs radical anion.

### 3. Conclusions

In conclusion, TCIPDI dianion salt was easily prepared under mild conditions with the simplest and most feasible process. The TCIPDI dianion salt showed a maximum UV—vis absorption peak at 610 nm together with a weak fluorescence emission peak at 763 nm. When titrated with hydrochloric acid, acetic acid, terephthalic acid or concentrated nitric acid and oxidizing metal ions in low concentration, the UV absorption spectrum remained essentially unchanged. However, when titrated with NaOH aqueous solution, the UV absorption spectrum had undergone tremendous changes: TCIPDI dianion changed into radical anion and neutral TCIPDI. Furthermore, TCIPDI dianion salt dissolved in different

solvents had exhibited the same optical characteristic band of the dianion. And that is to say TCIPDI dianion salt was high stable to acid, solvent and oxidizing metal ion, nevertheless, on the contrary, the dianion changed slowly into corresponding radical and neutral perylene diimide in alkali solutions.

### 4. Experimental section

### 4.1. Material

Materials: All reactions were carried out under an argon atmosphere. All chemicals were purchased from commercial sources (Aladdin) and used without further purification, including DMF, unless otherwise mentioned.

### 4.2. Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz Spectrometer with CDCl<sub>3</sub> as solvent and tetramethysilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectrum was recorded with the KBr pellet technique within the 400 to 4000 cm<sup>-1</sup> on a Perkin-Elmer spectrum 100 spectrophotometer. UV-Vis spectra was performed with a Perkine Elmer Lambda 35 spectrophotometer in DMF solution at room temperature. Fluorescence spectra was measured on PE LS-55 system in DMF solution at room temperature. Cyclic voltammetry measurements were performed in DMF solution, under argon atmosphere with a computer controlled CHI600E electrochemical workstation in a three electrode single-compartment cell using platinum electrodes and Ag/AgCl electrode as reference electrode, platinum dis electrode as working electrode, with Fc/Fc\* redox couple as internal standard, with a tetrabutyl-ammonium hexafluoro-phosphate (Bu<sub>4</sub>NPF<sub>6</sub>) solution (0.1 M) in DMF at a scan rate of 0.1 V/s.

### 4.3. Synthesis

### 4.3.1. Synthesis of TClPDI

The general procedure was employed using 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride (1.408 g, 2.656 mmol), the cyclohexylamine (1.21 mL, 10.55 mmol), and ethanol (20 mL) in a 50 mL round bottom flask equipped with a stir bar and sealed with a septum. The reaction vessel was purged with argon and subsequently heated with stirring at 80 °C for 24 h with reflux to stop the reaction. At the conclusion of the reaction, the vessel was allowed to cool to room temperature, the main content was dissolved in ethanol, and the filtrate was collected by filtration using a 0.8  $\mu$ m nylon membrane. Subsequently, the solvent was removed by rotary evaporation. The solid residue was then vacuum dried at 80 °C for 24 h.

Yield: 2.086 g (3.023 mmol, 85%) orange solid. FI-IR (KBr, cm<sup>-1</sup>): 2926 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 1376 cm<sup>-1</sup> (-CH<sub>2</sub>-); 1703 cm<sup>-1</sup> (C=O); 1663 cm<sup>-1</sup> (-CO-N-); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ):  $\delta$  = 8.658 (S, 4H, Per-H Per-H), 5.02-5.06 (t, 2H, *J* = 8 Hz, -N-CH-(CH<sub>2</sub>)), 1.49-2.57 (m, 20H, -CH<sub>2</sub>-); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ) 162.66, 135.28, 132.89, 131.39, 128.38, 123.74, 123.32, 54.43, 29.73, 29.08, 26.48, 25.33. Anal. Calcl (%) for: C<sub>36</sub>H<sub>26</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.45; H, 3.78; N, 4.05; Found C, 62.48; H, 3.75; N, 4.03%. UV/Vis (DMF, 5 × 10<sup>-5</sup> M, 298 K):  $\lambda_{max}$ /nm ( $\epsilon$ /M<sup>-1</sup>cm<sup>-1</sup>) = 518 (16000), 482 (10719).

### 4.3.2. Synthesis of TCIPDI dianion salt

A mixture of TCIPDI (0.704 g, 1.328 mmol) and DMF (20 mL) first undergone stirring on a magnetic stirrer thermostat for 10 min at room temperature. Then, potassium carbonate (0.366 g, 2.656 mmol) was added as a catalyst and the temperature was adjusted to 85 °C and kept for 8 h with reflux. After the reaction, the solvent was removed by rotary evaporation. The solid residue was thoroughly washed with enough water and then was vacuum dried at 80 °C for 24 h. Then, the crude product was dissolved in eluent [V (dichloromethane):V (petroleum ether) = 2:1] and purified by column chromatography on silica 200–300 to afford the TCIPDI dianion salt.

Yield: 0.856 g (0.237 mmol, 80%) navy blue solid. FI-IR (KBr, cm<sup>-1</sup>): 2923 cm<sup>-1</sup>, 2854 cm<sup>-1</sup>, 1376 cm<sup>-1</sup> (–CH<sub>2</sub>–); 1700 cm<sup>-1</sup> (C= O); 1649 cm<sup>-1</sup>, 1637 cm<sup>-1</sup> (–CO–*N*–), 1557 cm<sup>-1</sup> (Per-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ):  $\delta$  = 8.496 (S, 1H, Per-<u>H</u>),  $\delta$  = 8.345 (S, 1H, Per-<u>H</u>),  $\delta$  = 7.436 (S, 1H, Per-<u>H</u>),  $\delta$  = 6.845 (S, 1H, Per-<u>H</u>), 5.04–5.09 (t, 2H, *J* = 8 Hz, –*N*–CH-(CH<sub>2</sub>)), 1.43–2.62 (m, 20H, –C<u>H</u><sub>2</sub>–); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ) 170.09, 163.60, 163.36, 147.22, 139.20, 135.11, 134.00, 132.80, 131.35, 129.90, 129.83, 126.90, 125.89, 123.14, 119.20, 115.51, 112.03, 109.94, 55.99, 49.82, 32.97, 32.19, 29.73, 24.52. Anal. Calcl (%) for: K<sub>2</sub>[C<sub>36</sub>H<sub>26</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>]: C 56.11, H 3.40, N 3.64; Found: C 56.54, H 3.48, N 3.40. UV/Vis (DMF, 5 × 10<sup>-5</sup> M, 298 K):  $\lambda_{max/nm}$  ( $\epsilon$ /M<sup>-1</sup>cm<sup>-1</sup>) = 610 (11007).

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2017.10.013.

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