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Note

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# Visible Light-triggered Generation of Ultra-stable Radical Anion from Nitro-substituted Perylenediimides

Vikas Sharma, Unnikrishnan Puthumana, Pirudhan Karak and Apurba Lal Koner\*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal-462066, Madhya Pradesh, INDIA

Supporting Information Placeholder



**ABSTRACT:** An efficient method for visible light-triggered generation of radical from mono and dinitro-substituted Perylenediimide (PDI) derivatives is developed. UV-Vis.-NIR and EPR measurements were carried out to confirm the formation of radical. Most importantly, these radical anions were remarkably stable for several months. Subsequently, the reversible nature of anions was validated by both chemical and spectroelectrochemical methods for the application in electrochromic materials.

Over the past few years, there has been a steadily growing interest in making stable organic radicals.<sup>1-5</sup> Redox-active radicals have found applications in photovoltaics,<sup>6</sup> organic electronics,<sup>7-13</sup> and catalysis.<sup>3, 14-15</sup> Modulation of electronic properties by changing the substitutions, we can fine-tune the radical properties and efficiency of organic radical generation. Photo-triggered generation of metal-free organic radicals is a key-advancement towards developing efficient photo-catalysts and solar cells.<sup>3</sup> The radical generation efficiency, kinetics, and its stability in ambient conditions are equally important. However, only limited number of purely organic compounds are known to possess such qualities.<sup>5</sup> Particularly, perylenediimide (PDI) dyes, an important class of rylene dyes, known for their high brightness and exceptional stability are promising candidates for generating organic radicals.<sup>16-18</sup> Mostly, the stability of the radicals generated from PDI is attributed to the presence of electron withdrawing imide groups. Hence, incorporation of additional electron-withdrawing groups can lower the reduction potential and enhance their radical stability.

In this direction, Wasielewski and co-workers reported a series 50 of electron deficient PDI with cyano and trifluoromethyl 51 groups in the bay region to stabilize radical anions.<sup>19-20</sup> 52 Rybtchinski group synthesized a water-soluble PDI derivative 53 with polyethylene glycol chains at the imide positions and 54 generated its dianions using Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> as a reducing agent.<sup>21</sup> 55 Furthermore, Würthner group has developed ambient stable 56 PDI dianion-disodium salt and zwitterionic PDI-centered radi-57 cal anion.<sup>22-24</sup> Interestingly, the generation of ambient-stable 58

radical anions by reducing a pentafluoro-phenoxyl-substituted PDI was also reported.<sup>25</sup> Recently, a supramolecular strategy is explored for stabilizing PDI radical anions and for their application in photo-thermal therapy.<sup>26-28</sup> Moreover, the ease of conversion and stability of the radical anions from *bay*-halogenated PDI derivatives are shown to be much better than that of non-halogenated. Similarly, the chlorinated PDI showed a stronger effect compared to brominated PDI. With this realization, we explored the potential of highly electron withdrawing nature of nitro group for stabilizing the radical anion originated from mono (1) and di-nitro (2) substituted PDI. Although a class of nitro-substituted PDI had been reported,<sup>29</sup> to our best knowledge, generation of radical anions on these nitro-substituted PDIs and quantification of the role of visible light in this process is still unexplored.

Herein, we have demonstrated a facile generation of visiblelight triggered ultra-stable organic radical anions from two nitro-substituted PDI derivatives (see Scheme 1). Various spectroscopic and electrochemical techniques such as UV-Vis.-NIR, EPR spectroscopy, and spectroelectrochemistry were employed to characterize the radical anions. The photogenerated radical anions were stable for several months under ambient conditions. Further, the chemical and electrochemical reversibility was verified using various reducing and oxidizing agents and by spectro-electrochemistry. Scheme 1. Chemical structures of mononitro-substituted PDI (1) and dinitro-substituted PDI (2) and schematic representation of the reversibility of visible light triggered radical generation



After synthesis and characterization of 1 and 2 using modified protocol (see experimental section and Figure S1-5), the reduction of both dyes, 1 and 2 in DMF at the different time with visible light exposure were monitored using UV-Vis.-NIR spectroscopy (Figure 1). The reduction was found to proceed in dimethyl formamide (DMF) even without the addition of any additional reductant. The solution of 1, initially red in color, turned into light-green (Figure 1c, Scheme S2) as it was exposed to visible daylight, due to the presence of electron rich N,N-dimethyl amine in DMF because of its decomposition. The prerequisite of light and the presence of amine have been verified using freshly distilled DMF and addition of sacrificial amine such as N,N-diethylamine (DEA, see Figure S6-9). The calculated excited-state oxidation potential of  $1^{-1}$ and  $2^{-}/2$  is 1.74 V and 2.01 V respectively (see experimental section). Higher excited-state oxidation potential of compound 2 in comparison to 1 is reflecting that its oxidation of is difficult compared to 1 in the excited-state. Similarly, solution of 2 in DMF also changed from red to olive-green (Figure 1d) only upon exposure to visible daylight.



**Figure 1.** Monitoring radical-formation using UV-Vis.-NIR absorption spectroscopy: (Top) The electronic absorption spectra of radical-formation from 50  $\mu$ M of (a) 1 and (b) 2 in DMF. (Bottom) Formation kinetics and visible color change; plot of absorbance at 680 nm against exposure time for (c) 1 and (d) 2 to visible daylight. Inset shows a visible color change of the solution due to radical formation.

The UV-Vis. spectrum of **1** shows characteristic peaks around 520 and 485 nm (see Figure 1a) however, upon exposing to visible light the characteristic peaks of  $1^{-1}$  (at 680, 500 and 425 nm) appeared.<sup>30</sup> The characteristic peaks of  $1^{-1}$  conferred the single-electron transfer process from *N*,*N*-dimethyl amine present in DMF to excited **1** and the conversion was complete within 10 min. The reduction of **2** also followed a very similar kinetic and spectral feature (Figure 1b and 1d). As shown in Figure 1b, peak at 520 nm disappears and a set of peaks at 680, 525 and 420 nm appear as is  $2^{-1}$  formed. Moreover, the occurrence of isosbestic points in multiple wavelengths also suggests the co-existence of only dye and photogenerated radical anion species in solution.

Subsequently, to confirm the generation of radical anions, we have performed electron paramagnetic resonance (EPR) spectroscopy and it provided the unequivocal evidence of  $1^{-}/2^{-}$ . In DMF, radical anion formed from 1 gave a peak at 3350 G (Figure 2a) with a g-factor of 2.01. While the radical anion formed from 2 also gave a similar peak at around 3355 G (Figure 2b) with a g-factor of 2.01. Further to assess the stability of the radical anion in ambient conditions, in the UV-Vis.-NIR spectra of  $1^{-}/2^{-}$  solutions were monitored for several months (see Figure 2c and 2d). The absorbance intensities at 680 nm were plotted against time in days. Interestingly, no change in the peak intensity was observed even after monitoring for 40 days. The occurrence of multiple isosbestic points further confirms that ultra-stability of the photogenerated radical anions. The extra-stability is thought to be due to the presence of the highly electron-withdrawing nitro group in the bay position, stabilizes the formation of radical anions.



Figure 2. (Top) Confirmation of radical by EPR spectroscopy; EPR spectra of radicals formed from 1 mM of (a) 1 and (b) 2 in DMF. Peaks centered around 3350 G is indicating the unmistakable presence of the paramagnetic radical anion species. (Bottom) Super-stable radicals; Absorption spectra of (c) 1 and (d) 2 in DMF in the course of 40 days. Inset shows the plot of absorption at 680 nm with time. The intensity has not decreased significantly even after 40 days verifying the super-stability of the radical anions in the solutions

The reduction of **1** was further explored in other solvents by addition of various well-explored reductants.<sup>30</sup> An efficient and photo-triggered radical generation using 1 equivalent of

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tetrabutylammonium fluoride (TBAF) in various solvents such as toluene, THF, and chloroform is shown in Figure S10-12. To verify, the role of TBAF in the reduction process, we have performed <sup>1</sup>H NMR experiment and obtained unidentified peaks (Figure S13) hinted a complicated reduction mechanism as indicated recently.<sup>31-33</sup> It shows that the emerging peak intensity at 680 nm which gets saturated within 15 min in DMF, chloroform, and THF (Figure 1 and S10a-b) while it took *ca.* 30 minutes to get the saturation in toluene (Figure S7c). This could be due to non-polar nature of toluene, which would be unfavorable to the forming radical.<sup>22</sup>

Also, by addition of higher equivalent of reductant in toluene showed no considerable increase in the peak intensity, indicating that the conversion was completed by the use of just one equivalent of TBAF (Figure S11). The relative percentile of radical formation of 1 in different solvents is assessed (Figure S12). As it can be seen from Figure S12, in toluene, the percentage conversion is significantly low. However, in other solvents such as THF, DMF and chloroform, addition of higher equivalents of strong TBA bases resulted in a dianionic state. Further, this was confirmed by spectroelectrochemistry measurements (vide infra.). To assess the reduction process by various other reductants were also examined (Figure S14-15). Interestingly, the reduction was also found to be happening even with a weak base TBACN (Figure S15). Likewise, the reduction of 2 was also carried out in both DMF and chloroform in addition of other reductants (see SI).



Figure 3. (Top) Switchability between 1 and  $1^{--}$  UV-Vis.-NIR absorption spectra of MNPDI in DMF upon applying different potentials. Corresponding color changes in solution taken in cuvettes are also shown in different time intervals. (Bottom) Chemical oxidation: Absorption spectra of radicals generated from (b) 1 and (c) 2 before and after addition of NOBF<sub>4</sub> in chloroform.

To understand the electrochemical properties of 1 and 2 and their radical anion, we have performed cyclic voltammetry (Figure S16-18). Cyclic voltammogram of radical generated from 1 (Figure S17) shows a reversible reduction peak at *ca*. –

0.7 V indicating a possibility of further second reduction. This would suggest that a dianionic state could be formed by further reduction of the radical anion. Thus, we tried to chemically generate the dianionic state from 1 using tetrabutylammonium hydroxide (TBAOH). Surprisingly, the dianionic state was formed by addition of just two equivalent of TBAOH in THF whereas no others have reported the formation of dianions using such low concentrations of reductants (see SI, Figure S19), which is also corroborating its high electron affinity. The formation of this dianionic state from a radical state is associated with a visible color change in solution from green to blue (see Figure S20). Further, we tried to generate dianions in various solvents such as DMF, chloroform and toluene (Figure S19). The formation of blue color dianionic state from green color radical anionic state has been associated with a hypsochromic shift in absorption peak from 680 nm to 600 nm. The peak at around 600 nm thus could be attributed as the dianionic state.22

However, the dianionic state was found to have not formed in toluene which could be again due to the unfavorable thermodynamics of formation in a highly non-polar toluene as shown earlier.<sup>30</sup> The cyclic voltammogram of 2<sup>•</sup> however, did not show any such distinguishable oxidation peaks (Figure S15b). As a result, dianion of 2 was not found to have formed even upon treating 2 with greater equivalents of reductants. To get a better insight, spectroelectrochemistry was performed on both 1 and 2 to study the changes in absorption spectra upon applying potentials (Figure 3). Upon applying the negative potential (-0.64 V) to 1, the peak 520 nm disappeared and a new spectrum emerged with a characteristic peak at 680 nm (Figure 3a and S21a). This was accompanied by a change in the color of solution from red to green, similar to what we have already observed in chemical reduction. This confirms that the electrochemical reduction of 1 results in the same radical compound as the chemical reduction. Also, upon applying a positive potential of +0.35 V, the solution changed its color from green to red. Also, a shift in peak was observed from 680 nm to 520 nm, indicating regeneration of 1 by oxidation of radical. Further, to validate the reversibility in the switching, we have performed two rounds of reduction/oxidation cycles on 1 using spectroelectrochemistry (Figure 3a). Such reversibility of PDI dyes might be crucial in various applications such as switches. Similarly, upon electrochemically reducing 2, peak at 520 nm disappeared and peaks characteristic to radical anion appeared at 680, 525 and 420 nm upon applying a potential of -0.34 V (Figure 3a and S21b). Color of the solution changed from initial red to olive green. Further, when a potential of +510 mV was applied, the peaks at 680, 525 and 420 nm started to diminish and a peak at 520 nm appeared with dominating intensity. A visible color change from olive green colored solution to red was also observed. The peak at 520 nm is characteristic to 2 and its re-appearance confirms the oxidative regeneration of 2 from its radical anion. Since, both 1 and 2 could be easily switched between radical and neutral state by using electrochemical techniques, the PDI-reductant interaction can be thought as purely electrochemical in nature. Therefore, we have fabricated a prototype of an electrochromic device (ECD, Figure S22). The electrochemical reversibility also opens up the possible chemical reversibility, we tried chemically reversing the reduction of both 1 and 2 using a strong oxidant nitrosonium tetrafluoroborate (NOBF<sub>4</sub>). As shown in Figure 3b-c, we were able to generate back the characteristic peak of both 1 and 2 by just using 1 equivalent of NOBF<sub>4</sub>. Notably, this correlation between reversible spectro-electrochemical and chemical reduction suggests that the said reduction is a one-electron transfer process involving no covalent bond formation.

In conclusion, two nitro-substituted PDI derivatives were successfully synthesized for the generation of visible-light triggered ultra-stable organic radical anions. The generated radical anions were found to be stable in solutions for months. The paramagnetic nature of radical anions was confirmed through EPR spectroscopy and spectroelectrochemical investigations. The radical anions were efficiently generated *via* simple reductants or electron-rich solvent such as DMF. This study on reversible charging of simple nitro-substituted PDI dyes with ultra-stability will surely be an important addition to radical chemistry; visible-light mediated organic photocatalysis and an omnipotent extension to the field of organic electronics.

# EXPERIMENTAL SECTION

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Steady-state absorption spectroscopy. Steady-state absorption measurements, if not otherwise mentioned were performed using Cary 5000 Spectrophotometer from Agilent Technologies using 1 cm path length quartz cuvette. Samples were taken at a concentration of 50  $\mu$ M if not mentioned otherwise. Scan rate used was 400 nm/min. and sample interval, 0.667. Absorption measurements required for spectroelectrochemistry were measured using an HR 4000 spectrophotometer from Ocean Optics along with a 1 cm cuvette holder and DT-MINI-2-GS UV-Vis.-NIR lightsource. All the experiments were carried out at ambient temperature (298 K) if not otherwise stated. The intensity was measured by LX-101 lux meter by Lutron. As there was no change in spectrum upon keeping the solution inside the spectrophotometer, it was exposed to light for short time-periods between the measurements. These time periods are termed as the 'exposure-time'.

**Electron paramagnetic resonance spectroscopy.** The samples required for EPR spectroscopy were prepared in DMF at 1 mM concentration and measurements were done at 140 K temperature. Modulation amplitude was set to 1 and time constant 24.

**Cyclic voltammetry.** Cyclic voltammetric measurements were taken using an electrochemical analyzer of CH Instruments. Working electrode used was Pt along with an Ag/AgNO<sub>3</sub> reference electrode and Pt counter electrode. For the measurement, 1 mM of both 1 and 2 were dissolved in DMF. Supporting electrolyte used was tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>).

**Calculation of the excited-state oxidation potential of 1 and 2.** The excited-state oxidation potential of **1** and **2** is calculated according to the Rehm-Weller equation<sup>34</sup> using a reduction potential value of -0.64 V vs SCE (**1**•/**1**) and -0.37 V vs SCE (**2**•/**2**) in DMF. The  $E_{0-0}$  transition energy of *ca.* 2.38 eV is calculated at 520 nm (from the absorption maxima as compound **1** and **2** both are non-fluorescent). Taking these two values in account, the excited-state oxidation potential in the e is expected to be +1.74 V for **1** and +2.01 V for **2** vs SCE.

**Spectroelectrochemistry.** Absorption spectra were taken using an HR 4000 spectrophotometer developed by Ocean Optics along with a 1 cm cuvette holder and DT-MINI-2-GS UV-Vis-NIR lightsource. A CH electrochemical analyzer was used to hold the samples at desired potentials. A Pt working electrode, Ag/AgNO<sub>3</sub> reference electrode and a Pt counter electrode were also used for this purpose. Supporting electrolyte

used was 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF $_6$ ).

**Mass Spectrometry.** All mass spectrometric data were recorded using atmospheric pressure chemical ionization (APCI) on MicroTOF-Q-II mass spectrometer using chloroform as a solvent.

### 2,9-dicyclohexyl-5-nitroanthra[2,1,9-def:6,5,10-

d'e'f'ldiisoquinoline-1,3,8,10(2H,9H)-tetraone 1: Under open air, PDI (100 mg, 0.18 mmol), Sodium nitrite (15 mg, 0.22 mmol), nitric acid (520 µl,12.45 mmol), was added in 30 ml dichloromethane and stirred at room temperature for 4 h. After that the reaction mixture was neutralized with 15% KOH solution and extracted with chloroform. The crude product was purified by silica gel column chromatography using eluent as dichloromethane afforded the pure compound 1 as an amorphous solid (90 mg, 83.25 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.74 (d, J = 8.0 Hz, 1H), 8.71 - 8.62 (m, 4H), 8.55 (d, J =8.1 Hz, 1H), 8.17 (d, J = 8.1 Hz, 1H), 5.02 (t, J = 12.1 Hz, 2H), 2.54 (q, J = 12.4 Hz, 4H), 1.92 (d, J = 11.3 Hz, 4H), 1.77 (d, J = 11.3 Hz, 6H), 1.52 - 1.29 (m, 6H). <sup>13</sup>C NMR (126) **MHz, CDCl<sub>3</sub>**) :  $\delta$  = 163.6, 163.3, 163.2, 162.3, 147.7, 135.4, 132.9, 132.9, 131.4, 131.2, 129.4, 129.4, 129.0, 128.0, 127.6, 126.6, 126.5, 126.4, 125.5, 124.8, 124.6, 124.1, 123.7, 54.6, 54.4, 29.3, 29.2, 26.7, 26.6, 25.5, 25.5. HRMS (APCI) m/z:  $[M+H]^+$  Calcd for C<sub>36</sub>H<sub>30</sub>N<sub>3</sub>O<sub>6</sub> 600.2056 Da; Found 600.2135 Da.

### 2,9-dicyclohexyl-5,12-dinitroanthra[2,1,9-def:6,5,10-

d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone 2: Under nitrogen atmosphere, compound 1 (400 mg, 0.67 mmol), cerium (IV) ammonium nitrate (800 mg, 1.46 mmol), nitric acid (5 ml, 79.36 mmol), was added in 100 ml dichloromethane and stirred at room temperature for 48 h. After that the reaction mixture was neutralized with 15% KOH solution and extracted with chloroform. The crude product was purified by silica gel column chromatography using eluent as dichloromethaneafforded a mixture of 1,7- and 1,6-dinitroperylene bisimides and after analysis of <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) it was found in the ratio of 3:1. By repetitive crystallisation pure 1,7dinitroperylene bisimide was obtained as an amorphous solid 2 (150 mg, 35 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.80$  (s, 2H), 8.64 (d, J = 8.0 Hz, 2H), 8.31 (d, J = 8.0 Hz, 2H), 5.01 (m, 2H), 2.57 - 2.45 (m, 4H), 1.92 (s, 4H), 1.75 (d, J = 11.5Hz, 6H), 1.34 (d, J = 12.5 Hz, 4H). HRMS (APCI) m/z:  $[M+H]^+$  Calcd for  $C_{36}H_{28}N_4O_8$  645.1907 Da; Found 645.1959 Da

Fabrication of a prototype ECD device. Since the spectroelectrochemistry proves that 1 and 2 can be electrochemically switched between radical and neutral states, this reveals a possible application of these PDI dyes in fabricating certain electrochromic materials. Here, we mix coat a mixture of 1 and polymethyl methacrylate (PMMA) on an Indium tin oxide (ITO) and examine if this film exhibits a change in color upon application of potential. For the fabrication of this device, 1 mM mononitro PDI was dissolved in a 33:53:14 w/w mixture of PMMA, propylene carbonate (PC) and TBAPF<sub>6</sub> in THF.<sup>35-36</sup> Mixture was tightly closed and stirred for 24 hours. Then, this mixture was drop-casted onto an ITO film to create a colored conducting layer. This ITO was then dipped in an electrolyte solution and potential was applied to it. Upon application of potential, instantaneously the red colored film coated on ITO turned dark, with greenish trace inside it (Figure S19). This greenish trace could be attributed to the formation of radical 1

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anions and the remaining dark red traces to the remaining, unconverted neutral **1**.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The synthetic scheme, other spectroscopic, electrochemical characterization, and prototype electrochromic device are given *via* a link at the end of the document. (file type, i.e., PDF)

# AUTHOR INFORMATION

#### 12 Corresponding Author

13 E-mail: <u>akoner@iiserb.ac.in</u>

ORCID: 0000-0002-8891-416XX

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