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Modulation of internal charge transfer (ICT) in a bay region hydroxylated perylenediimide (PDI) chromophore: a chromogenic chemosensor for pH

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Abstract—A novel perylenediimide derivative which has a bay region hydroxyl function behaves as a pH-sensitive dye. The deprotonation of the aryl-OH yields a green solution with a $\lambda_{\max}$ of 692 nm and this deprotonated form has strong internal charge transfer characteristics. On reprotonation in acidic solutions, the typical PDI absorbance spectrum is restored. The experimentally determined pK_a (7.45) is very close to physiological pH, therefore the most significant changes in color take place in the vicinity of this pH value.

Rational design of molecular reporters of ion concentrations is a very active field of research. A number of photophysical processes can be exploited to yield observable parameters which can be correlated to the analyte concentration. Progress in these areas has been reviewed.[1] It is clear that if an internally referenced signal (ratiometric signal) is required, a significant spectral shift in either the absorption or emission spectra becomes very important. The most straightforward way to guarantee such a spectral change is to design an internal charge transfer dye with strong electron donor and acceptors within the same molecule. In these ICT chromophores, both the donor and the acceptor groups are parts of the same π-system. Thus, when an analyte interacts with either a donor or acceptor part of the dye, a significant spectral shift results.

Perylenediimides are known as dyes and pigments of high stability and high quantum yields in solution. They have found applications in many fields including organic light emitting diodes,[2] molecular switches and wires,[3] light-harvesting arrays,[4] photoreactive thin films,[5] solar cells,[6] and dye lasers.[7] In recent years, bay region functionalized PDI dyes became available with improved solubility and potential for further derivatization and novel applications.[8] 1,7-Dibromoperylenediimides proved to be a gateway to a number of donor substituted PDI dyes at the bay region. Amine substitution at these positions typically yields dyes of long wavelength absorption and weak long wavelength emission,[9] which are not affected by the addition of acids such as TFA.

As a part of our research program, whilst carrying out a systematic study of heterocyclic amine substitutions at the bay region, we noticed that a novel fluorophore with bright red fluorescence was obtained during these reactions, and this side product appeared in all the reactions and proved to be independent of the amine used. In order to elucidate the structure and to study its properties, we optimized the reaction conditions to maximize the yield of this novel fluorophore (Scheme 1). Thus, when **1** was heated with glycine *tert*-butyl ester in BuOH–H_2O in the presence of Et_3N at 90 °C for 18 h, the corresponding PDI dye **2** was obtained in good yield (75%). Then, this compound was treated with *N*-methylpiperazine in NMP at 85 °C for 24 h to yield the hydroxy-PDI **3** in a 25% isolated yield. The *tert*-butyl protecting groups could be quantitatively removed in TFA/DCM to yield the dye **4**. Satisfactory analytical data were obtained for all new compounds. The absorbance and fluorescence emission of the protected form **3** was studied in different solvents. In chloroform, compound **3** has two peaks at 520 and 555 nm

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Keywords: Chemosensors; Perylenediimides; pH Sensing; Chromogenic sensor; Chromophore.

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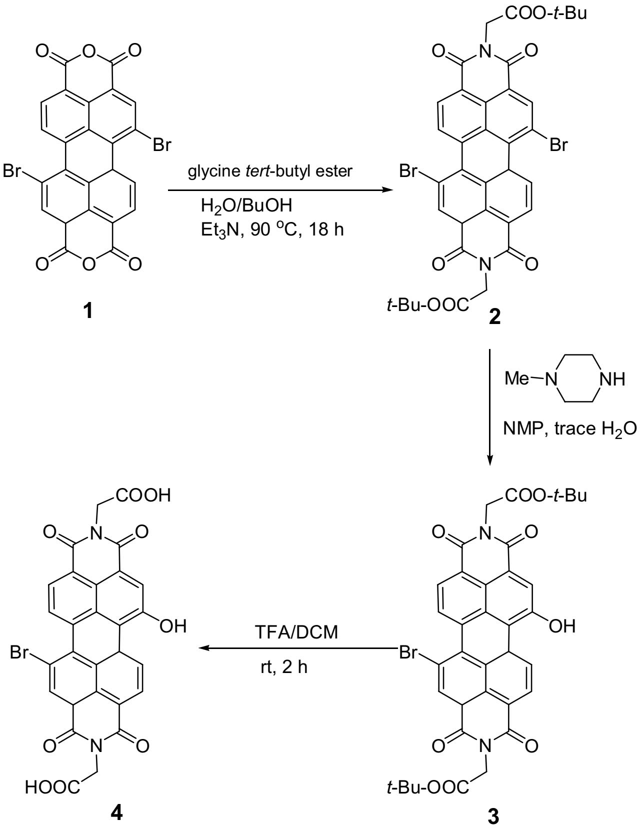

Scheme 1. Synthesis of a bay region hydroxylated PDI dye.

and a shoulder at 480 nm (Fig. 1). This spectrum is not that different from an ordinary PDI dye. However, the addition of Et_3N causes a remarkable change in the color of the solution (from orange-red to green) with a concomitant disappearance of the PDI emission. The new peak is now centered at 758 nm. It is broad and featureless, very much in accordance with internal charge transfer (ICT) characteristics. Naturally, the change is fully reversible, protonation of the Ar–O$^-$ by the addition of TFA restores the original color with bright red emission under ambient light.

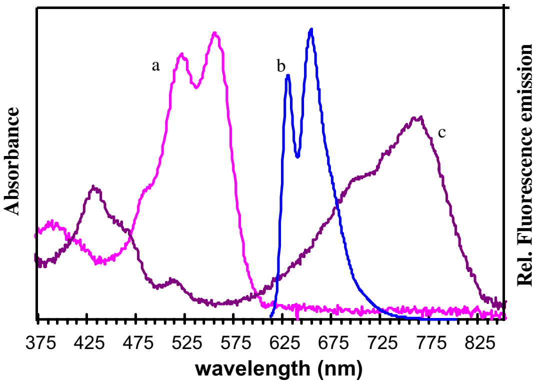

Figure 1. Absorption and emission spectra of compound **3** in chloroform: (a) absorbance, (b) emission, (c) absorbance with the addition of a drop of triethylamine.

The deprotected dye is moderately water soluble at neutral pH, but shows tendency to aggregate on standing. For this reason, the spectral characterization of this compound was carried out in 50:50 ethanol–aqueous buffer solutions. Absorption spectra (Fig. 2) were obtained in a series of solutions with varying buffer pH in the range of 6.5–9.0. Deprotonation of the arylhydroxy function results in clean isosbestic points (458 nm and 585 nm, excluding the lowest pH value, which shows signs of aggregation) in the absorption spectra. From these changes, we can calculate a pK_a of 7.45, which happens to be very close to physiological pH values. In aqueous solution mentioned above, no emission was detected either from the protonated or deprotonated species. Hence, this derivative turns out be a chromogenic sensor of pH. The color change is clearly shown in Figure 3, a digital photograph of the solutions under ambient light. The color of the aqueous solutions is transformed gradually from reddish pink to green as the pH is increased. Thus, we have demonstrated that bay region hydroxylated PDI dyes can act as pH-sensitive chromogenic chromophores which signal pH changes around neutrality. Donor group substituted PDI dyes appear to have potential in signalling pH via the modulation of photoinduced charge transfer. Appropriate functionalization is expected to yield dyes of improved water solubility. Work to this end is in progress in our laboratories.

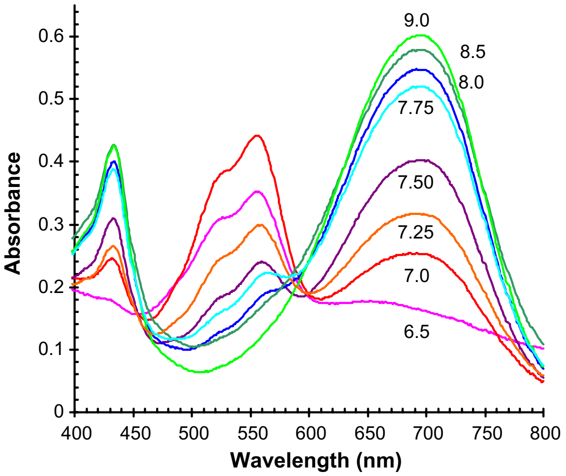

Figure 2. The absorption spectra of PDI derivative **4** in aqueous (50:50 EtOH–H_2O) buffer solutions of varying pH values. The solutions were buffered with 0.05 M MOPS (6.5, 7.0), HEPES (7.25, 7.5), TRIS (7.75–9.0). The concentration of the chromophore was 2.0×10^{-5} M.

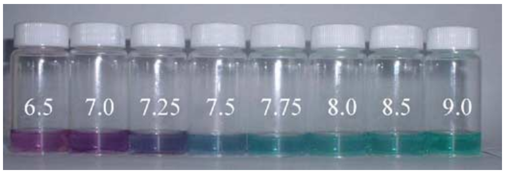

Figure 3. PDI derivative **4** in aqueous (50:50 EtOH–H_2O) buffer solutions of varying pH values under ambient light. The solutions were buffered with 0.05 M MOPS (6.5, 7.0), HEPES (7.25, 7.5), TRIS (7.75–9.0). The concentration of the chromophore was 2.0×10^{-5} M.

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References and notes

1. (a) Czarnik, A. W. *Chem. Biol.* **1995**, *2*, 423–428; (b) *Chemosensors of Ion and Molecule Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; NATO ASI Series, Ser. C492, 1997.(b) Valeur, B. *Molecular Fluorescence*; Wiley-VCH: Weinheim, Germany, 2002; (c) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566; (d) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M. *Coord. Chem. Rev.* **2000**, *205*, 41–57.
2. (a) Angadi, M. A.; Gosztola, D.; Wasielewski, M. R. *Mater. Sci. Eng. B* **1999**, *63*, 191–194; (b) Ranke, P.; Bleyl, I.; Simmerer, J.; Haarer, D.; Bacher, A.; Schmidt, H. W. *Appl. Phys. Lett.* **1997**, *71*, 1332–1334.
3. (a) Hayes, R. T.; Wasielewski, M. R.; Gosztola, D. *J. Am. Chem. Soc.* **2000**, *122*, 5563–5567; (b) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60–63.
4. Tornizaki, K.; Loewe, R. S.; Kirmaier, C.; Schwartz, J. K.; Retsek, J. L.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 6519–6534.
5. (a) Fuller, M. J.; Wasielewski, M. R. *J. Phys. Chem. B* **2001**, *105*, 7216–7219; (b) Fuller, M. J.; Walsh, C. J.; Zhao, Y.; Wasielewski, M. R. *Chem. Mater.* **2002**, *14*, 952–953.
6. (a) Gregg, B. A.; Cormier, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 7959–7960; (b) Breeze, A. J.; Salomon, A.; Ginley, D. S.; Gregg, B. A.; Tillmann, H.; Horhold, H. H. *Appl. Phys. Lett.* **2002**, *81*, 3085–3087.
7. (a) Sadrai, M.; Hadel, L.; Sauers, R. R.; Husain, S.; Krogh-Jespersen, K.; Westbrook, J. D.; Bird, F. R. *J. Phys. Chem.* **1992**, *96*, 7988–7996; (b) Gvishi, R.; Reisfeld, R.; Brushtein, Z. *Chem. Phys. Lett.* **1993**, *213*, 338–344.
8. (a) Dotcheva, D.; Klapper, M.; Mullen, K. *Macromol. Chem. Phys.* **1994**, *195*, 1905–1911; (b) Wurthner, F.; Thalacker, C.; Sautter, A. *Adv. Mater.* **1999**, *11*, 754–758; (c) Qu, J.; Kohl, C.; Pottek, M.; Mullen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1528–1531.
9. (a) Zhao, Y.; Wasielewski, M. R. *Tetrahedron Lett.* **1999**, *40*, 7047–7050; (b) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229–1233.