

NIR Absorption of Perylene Dyes and Fluorescence with Large Stokes' Shift by Simple Deprotonation

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

A brightly red fluorescent 1-hydroxypyrylene bisimide was prepared by a nucleophilic aromatic displacement reaction. The deprotonation of the hydroxy group shifts the absorption and the strong fluorescence into the NIR. A selected medium promotes an ESPT mechanism and induces a large Stokes' shift of nearly 200 nm in the NIR.

Key words: Dyes, Fluorescence Spectroscopy, NIR, ESPT, ESIPT, Perylenes

Introduction

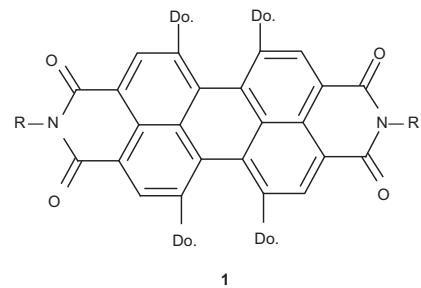
Chromophores [1] with light absorption at long wavelengths in the visible or even in the near infrared are becoming increasingly attractive [2]. Commonly, such a bathochromic absorption is realized with very large π systems; see for example ref. [3]. Bathochromically absorbing smaller molecules are more difficult to obtain [4], but can be developed by balancing substituent effects in conjugated π systems; compare ref. [5] and refs. therein.

The majority of dyes, such as the well-known triphenylmethane dyes consist of a central acceptor (Ac.) surrounded by π systems substituted with two donor groups (Do.) according to (1). The length of the π system and the donor and acceptor abilities determine the light absorption.



The interchanging of donor and acceptor groups such as in (2) would be equivalent to (1) for light absorption; see for example refs. [6–9].

The perylene bisimide chromophore with H instead of Do. in compound **1** corresponds to a duplicated ar-



angement according to (2). The carbonyl groups form the acceptors, however, the central donor according to (2) is lacking and thus, the light absorption is only moderately bathochromic. The introduction of donor groups into **1** in the positions 1, 6, 7, and 12 (Do. in **1**) such as phenoxy groups [10] or amino groups [11–13] causes an appreciable bathochromic shift. A further amplification of the donor properties by the α effects shifts the absorption as far as to the NIR region [14]. On the other hand, a strong bathochromic shift obtained with a single donor group would be of interest. A tuning of such a group would result in a color switch, and it thus represents a good functional unit for the construction of molecular devices.

Results and Discussion

We started for the preparation of tuneable dyes with the perylene tetracarboxylic bisanhydride and condensed it with 1-hexylheptylamine to obtain **2** (Scheme 1), where the long-chain secondary alkyl group (“swallow-tail substituent”) [15, 16] renders the material soluble. A single aromatic nucleophilic displacement reaction with the combination of DMSO and sodium methanolate was successful to form **3** [17]; no initial bromination [18] was necessary. The dipolar aprotic solvent forces the nucleophilicity of anions and also acts as a moderate oxidant to support the formal leaving of a hydride anion in this Tschitschibabin-analogous reaction. The oxidative support of the solvent can be monitored by the evolution of dimethyl sulfide. Molecular oxygen is also involved because no reaction is observed under argon atmosphere. Transient absorptions at $\lambda = 670$ (1.0), 622 (0.6 sh) and 528 nm (0.5) are observed and may be caused by a Meisenheimer complex. This may form either the starting material back again in the absence of oxygen by hydroly-

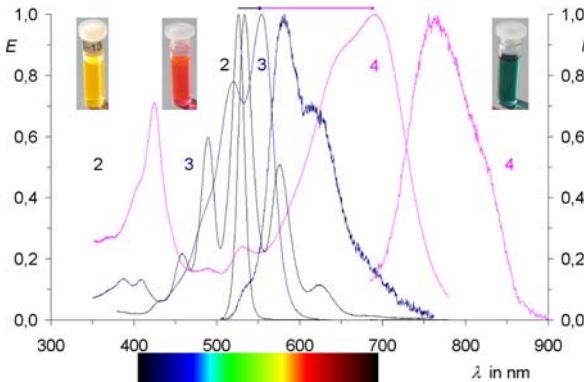


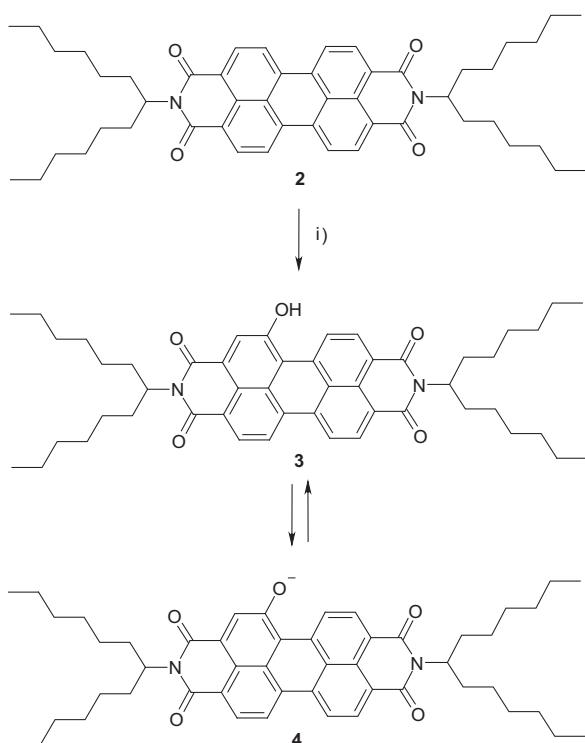
Fig. 1 (color online). UV/Vis absorption (E , each left) and fluorescence spectra (I , each right) of **2** (black), **3** (blue) and **4** (pink) in chloroform. Compound **4** with the addition of small amounts of DBU.

sis, or the phenolate anion **4** in the presence of oxygen. A second substitution of **3** and **4** is disfavored because the aromatic core becomes more electron-rich by the first one. Other nucleophiles such as cyanide can be introduced in the same way, however, activate the aromatic core for a second substitution. The reaction becomes more difficult to control and the resulting mixtures are difficult to separate.

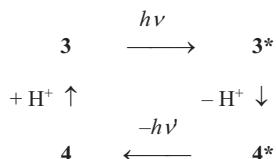
An appreciable bathochromic shift is induced by the hydroxy group in **3**, and an intense red fluorescence is obtained (Fig. 1).

The hydroxy derivative **3** is moderately acidic and can be deprotonated with bases such as DBU to form the anion **4**. This increases the electron-releasing properties of the donor appreciably. As a consequence, the UV/Vis absorption is shifted to the NIR region (Fig. 1). Remarkably, the anion **4** exhibits a strong fluorescence in the NIR so that it can be applied as a NIR fluorescent dye.

The acidity of **3** was determined by optical titration with diisopropyl ethyl amine where the absorption of the hydroxy compound decreases with increasing concentration of the amine (Fig. 2, left side) and the absorption of the phenolate increases (Fig. 2, right side). An isosbestic point is obtained between the two bands at about 480 nm; some deviations are caused by solvatochromism [19] because of the increasing amounts of the amine. The changes in the spectra in Fig. 2 can be analyzed by a coupling of acid-base equilibria, and a linear correlation is obtained if $E^2/(E_\infty - E)$ for the absorptivity E and the calculated absorptivity E_∞ for the pure compound **4** is plotted *versus* the concentra-



Scheme 1. Synthesis of the perylene dye **3**; i) NaOCH_3 , DMSO .



Scheme 2. Mechanism of the proton transfer according to Förster and Weller; $\mathbf{3}^*$ and $\mathbf{4}^*$ are electronically excited states of $\mathbf{3}$ and $\mathbf{4}$, respectively.

tion c of the added amine; see the insert of Fig. 2. The pK_a value for $\mathbf{3}$ is found to be 2.4 units higher than for diisopropyl ethyl amine calculated from the slope of this correlation and the absorptivity of $\mathbf{4}$: $\epsilon = 20\,500 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 682.02 nm. A pK_a value of 18.3 is calculated for $\mathbf{3}$ on the basis of the reported [20] pK_a value for diisopropyl ethyl amine in chloroform of 15.85. The use of $\mathbf{3}$ as a pH indicator for strongly basic media is of interest because of the absorption in the NIR so that even a strong coloration does not interfere with the measurements. A further extension for applications is given by the strong fluorescence of the anion.

Quantum chemical calculations (AM1) [21, 22] indicate that optical excitation induces a charge transfer from the hydroxy group to the aromatic nucleus. This causes an increase of the acidity of the phenolic group. A deprotonation of the excited state may proceed if a proper basicity of the medium is established. *N,N*-Dimethylaniline is a good candidate for such a deprotonation. 50% of the base in chloroform makes the deprotonation of the excited state of $\mathbf{3}$ dominating.

The absorption spectrum of $\mathbf{3}$ remains unaltered in this mixture except for a small solvatochromic effect, however, the fluorescence of $\mathbf{3}$ is nearly completely suppressed (Fig. 3). Instead, the fluorescence spectrum of $\mathbf{4}$ is obtained. The increase of acidity allows the phenol to proceed the kreisprozess of Scheme 2 according to the ESPT mechanism (Excited State Proton Transfer) described by Förster [23–25] and Weller [26] for the aqueous phase; for more recent reviews see refs. [27–29]. As a consequence, the Stokes' shift is increased to nearly 200 nm (4400 cm^{-1}) with an intense fluorescence in the NIR.

Light absorbing structures with such extremely high Stokes' shift are of interest for many applications such as dye laser and fluorescence planar concentrators [30] where the fluorescence light should not be re-absorbed by the dye. The large Stokes' shift is also of interest for analytical studies because intrinsic fluorescence of the background can be efficiently excluded in this way.

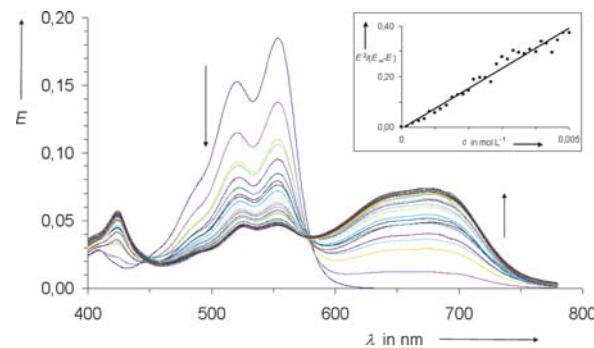


Fig. 2 (color online). UV/Vis absorption spectra of $\mathbf{3}$ in chloroform with increasing concentrations of diisopropyl amine in steps of 0.17 mmol L^{-1} up to a concentration of 5 mmol L^{-1} . Insert: Linear correlation of $E^2(E_\infty - E)$ as a function of the concentration c of ethyl diisopropyl ethyl amine for $\mathbf{3}$ in chloroform; E is the absorptivity at 682.02 nm, E_∞ is the absorptivity of $\mathbf{4}$. The square of the correlation number $R^2 = 0.971$ at $n = 31$ points.

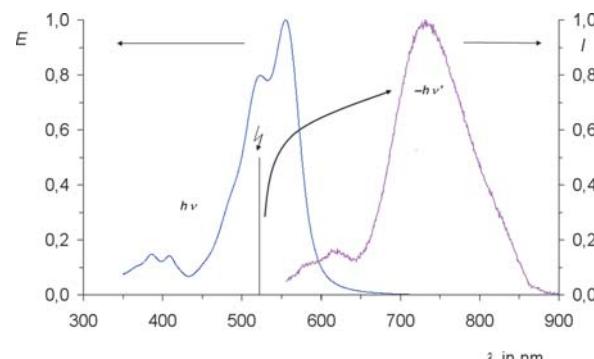


Fig. 3 (color online). Absorption- (blue, left) and fluorescence spectra (pink, right) of $\mathbf{3}$ in *N,N*-dimethyl aniline. Bar: wavelength of excitation for the fluorescence spectrum. A Stokes' shift of nearly 200 nm is obtained because of proton transfer according to Förster and Weller.

Experimental Section

2,9-Bis-(1-hexylheptyl)-1-hydroxyanthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3)

2,9-Bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (**2**, 108 mg, $142 \mu\text{mol}$) and sodium methanolate (34 mg, 0.63 mmol) were dispersed in DMSO (50 mL), heated with stirring (165°C , 6 h, evolution of dimethyl sulfide), cooled, treated with saturated brine (100 mL) and extracted with ether (300 mL). The organic phase was shaken three times with saturated brine (250 mL each), dried with sodium sulfate, filtered, evaporated *in vacuo*, and purified by medium-pressure chromatography

(800 mL silica 40...63 μm Merck Geduran, chloroform-ethanol 60 : 1, 40 mL \cdot min $^{-1}$). Yield 36 mg (33%), violet solid, m.p. > 250 °C. – R_f (silica gel, CHCl_3 -ethanol 80 : 1) = 0.10. – IR (ATR): $\tilde{\nu}$ = 3251.9 (w, br), 2953.3 (m), 2923.1 (vs), 2854.5 (s), 1692.3 (s), 1655.2 (m), 1634.2 (m), 1589.2 (vs), 1576.6 (s), 1511.0 (w), 1440.2 (w), 1418.1 (m), 1339.1 (s), 1320.3 (m), 1307.7 (m), 1263.2 (w), 1175.4 (w), 1120.6 (w), 975.6 (w), 938.0 (w), 862.7 (w), 845.1 (w), 808.1 (m), 748.0 (w), 723.3 (w), 612.2 cm $^{-1}$ (w). – ^1H NMR (600 MHz, CDCl_3 , 25 °C, TMS): δ = 0.81 (t, $^3J_{\text{H,H}} = 7.0$ Hz, 12 H, 4 \times CH_3), 1.21 – 1.34 (m, 32 H, 16 \times CH_2), 1.81 – 1.88 (m, 2 H, β - CH_2), 2.21 – 2.27 (m, 2 H, β - CH_2), 5.15 – 5.22 (m, 1 H, α -CH), 8.45 – 8.70 (m, 7 H, 7 \times CH-perylene), 9.63 ppm (m, 1 H, CH-perylene). – ^{13}C NMR (151 MHz, CDCl_3 , 25 °C, TMS): δ = 14.3, 22.8, 27.1, 29.4, 29.9, 32.0, 32.6 ppm. – UV/Vis (CHCl_3): λ_{max} (ϵ) = 517.5 (31000), 552.6 nm (42600). – Fluorescence (CHCl_3): λ_{max} (I_{rel}) = 578.0 (1.00), 619.5 nm (0.47 sh), fluorescence quantum yield ($\lambda_{\text{exc}} = 495$ nm, $E_{495\text{nm}} = 0.0832$ cm $^{-1}$, reference: **2** with $\Phi = 1.00$): 1.00. – HMRS: m/z = 770.4630 (calcd. 770.4659 for $\text{C}_{50}\text{H}_{62}\text{N}_2\text{O}_5$).

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